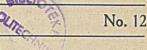
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## **EDITORIALS**

#### A VICTORY OF ARMS, NOT YET OF IDEALS

Thanks be to God, a new day has dawned! The forces of domineering might which at one time threatened to engulf the world have suddenly crumbled. Fantastic dreams of universal domination and worldwide loot have been dispelled by cold steel, high explosives, and the blood of those who believe in the brotherhood of mankind.

To those of our own and of our Allies who have made the great sacrifice of their lives our hearts turn first in this moment of victory. In spirit they will live forever honored among us. For those who soon will be returning a welcome awaits such as this country has never before given to any of its sons.

It is not yet possible to grasp the full meaning of the mighty events of the past month: the change is too stupendous. How far the actual change has progressed it is difficult now to tell. Certainly the military power of the Teuton has been crushed for generations; but has his heart been changed? We believe not. Has the Kaiser abdicated? We know not. Certainly no authentic publication of his abdication paper has appeared. The question has no military significance, but it has important bearing on the good faith of a nation which is now about to begin its elementary acquisition of this useful commodity; progress in this line cannot be made in his presence. Has defeat really been accepted by Germany? In a way, yes, but only in a way. The "solfings" of Dr. Solf, daily flashed to us by the wireless, show plainly that we are still facing the same German heart, have still to guard against the same machinations, have still to witness the same stupid psychology by which at onc time we as a nation were charitable enough almost to be deceived.

No, Germany has not yet gone down through the dark valley of suffering where alone she can cleanse herself for fellowship in the great family of nations. Until that day is reached let us be on our guard. The sacrifices already made for civilization must not be in vain.

#### NATIONAL SELF-CONTAINEDNESS

For the past four years we have advocated the doctrine of national self-containedness. The vast and varied natural resources of this country justify the conviction that economic independence can be attained if opportunity is afforded the chemist to exercise his skill upon this raw material. Lack of independence resulted not long ago in serious economic disturbances; preparedness for the future demands that recent progress toward independence, intensified by war conditions, continue unabated. Ultimate reaching of the goal depends upon two factors, our ability as chemists and the coöperation of the body politic.

The first of these two factors is our own responsibility; the second has for its foundations a sympathetic, well-informed public opinion, confidence in the ability of American chemists, patience to wait through the unproductive days of investigation, and willingness to meet perhaps higher costs of production during the period of development of research results into sound and efficient manufacturing practice. Without attempting a systematic survey let us make candid inquiry as to the present state of security of these foundation stones.

Certainly public opinion is to-day better informed and more sympathetic than ever before. So, too, is there abundant evidence not only of confidence but of pride in the ability of the chemist. The constant increase in the number of industrial research laboratories bears witness to increased willingness to wait upon investigation. So far so good. The last stone, however, the willingness to meet temporary higher costs of production, seems to be wabbly. Evidently an insufficient amount of cement has been used to give it firm setting. That some cement has been used is evidenced by the prompt action of consumers in joining in the request for a protective tariff in order to insure independence in dyestuff supplies. But what about potash and duty-free imports for educational institutions?

First, as to potash, real progress has been made in the procurement of a domestic supply, but support has not been received from the great organizations of the chief consumers, the farmers. Why is this? We will not attempt to answer, for it would bring us into the region of surmises. Perhaps a partial answer is found on page 2 of the U. S. Official Bulletin, October 25, 1918. Summarizing the conference on potash held in the offices of the Department of Agriculture, the Bulletin states:

"\*\*\* the view of the Department of Agriculture is that the Government should do all that is possible to encourage the production of potash from the cheapest sources in this country in order to enable farmers to obtain it at a low price, *because foreign supplies are now unavailable.*" (Italics are ours.)

The reading naturally suggests the thought, What will be the attitude when foreign supplies are again available? The cement is weak, very weak.

Second, at the Urbana meeting of the AMERICAN CHEMICAL SOCIETY the matter of "duty-free imports" for educational institutions was thoroughly discussed and a committee appointed to find some way of removing this obstacle to the development of American manufacture of laboratory supplies. Up to date, however, we have heard of no action by the Association of American Universities or by the heads of the chemistry departments of these institutions. Our constant plea is that Americans should stand by the American chemical industry. Should we not practice among ourselves what we preach to others? Moreover, can we put the right spirit into the students we are training for the American industry when the "import" atmosphere pervades the whole laboratory? This seeming saving through "duty-free imports" is one of the costliest endowments our educational institutions possess, in that it cuts at the very heart of independence through instilling the spirit of dependence in the chemists of the future.

#### A SPECIAL MEETING OF THE COUNCIL

At the outbreak of the war the AMERICAN CHEMICAL SOCIETY led the way in a prompt tender to the Government of a wealth of information, through the census of chemists and their qualifications, compiled in cooperation with the U. S. Bureau of Mines, which has proved of inestimable value. Now it is incumbent upon this great organization of American chemists to do its part in the reëstablishment of normal conditions. With this in view, there has been called a meeting of the Council of the Society at New York City on December 14, 1918, which will doubtless prove the most important in the history of that body. The Secretary's notice of the meeting contains the following salient paragraphs:

The Advisory Committee of the AMERICAN CHEMICAL SOCIETY has requested President Nichols to call a meeting of the Council at as early a date as practicable, in order that the Council may carefully consider the whole question of the Society's opportunity and duty in regard to the reconstruction of conditions chemical which are to follow after the war. The AMERICAN CHEMICAL Society has had an influence, fully admitted by all, during the war; and now that the war is over and peace is in sight other great problems are before us in the solution of which the Society can again serve our country.

can again serve our country. Accordingly, you are all asked to discuss these problems with the other chemists of your local section, or with anyone whose ideas are worth while, and to come to the meeting of the Council in New York prepared to present and elucidate your views. You are requested particularly to have a meeting of your local section called in advance of the Council meeting and to take up there with the members the general problem in order that the full force of the AMERICAN CHEMICAL SOCIETY may be felt in this matter.

You will find an interesting article by Dr. B. C. Hesse in the November issue of the *Journal of Industrial and Engineering Chemistry* which you should read. If possible, send to me in writing any ideas which may be evolved, to reach this office on or before December 10, in order that they may be brought before the Directors of the Society to be duly formulated with others in advance of the Council meeting.

Large problems loom before us which must be eonsidered from the new viewpoint which a world freed from the scourge of Teutonic ideas presents. No one man or small group of men is qualified to decide such matters. Decision must be based upon a thorough knowledge of the views of all chemists, presented and discussed where common counsel can be deliberately taken and policies carefully formulated.

Much material for discussion should be furnished in the suggestions received by the Philadelphia Section in response to their effective action following Dr. Hesse's address, "Preparation for After the War," published in our last issue. It should be borne in mind, however, that at that Council meeting any subject which bears upon the welfare of this country through chemistry is in order for discussion. Now is the time, therefore, for meetings of local sections, at which every phase of this subject should be canvassed, insuring thus that the gathering in New York City on December 14 will be thoroughly representative, not simply of the personnel, but of the views of the membership of the Society.

In this connection it should be noted that the Advisory Committee meets in the early part of each month, and that the committee would gladly welcome at any time suggestions from local sections, councilors, or individuals.

#### A GOLDEN OPPORTUNITY

As a Nation we have just expressed on Thanksgiving Day our gratitude that peace has been justly restored to a war-torn world. Again we approach that natal day whose century-old maxim is "Peace on earth, good will toward men." Shall these expressions of thankfulness and good will stop with mere lip service? We never wish it so, but often know not where to turn to find that human objective which will give to our sentiments the glorifying touch of personal application. On page 1024 of this issue Secretary Parsons outlines the work of the American Ouvroir Funds, which is seeking the "adoption" of those French orphans whose fathers were technical men, graduates of l'Ecole Polytechnique who have fallen at the front. The plan is so direct, so practical, and so filled with the human touch that it will grip the heart-strings of all who give it even a cursory reading.

The AMERICAN CHEMICAL SOCIETY has been asked to lend its aid in securing as many as possible of these "adoptions," which may be undertaken either by individuals or by groups. We are now in the midst of meetings of our local sections held for discussing constructive plans for the new period in the world's history into which we are about to enter. Could any more fitting prelude to these discussions be found than a warm-hearted presentation of the righteous claims of these orphans; could any nobler record appear upon the minutes of any local section than the statement of the number of these orphans "adopted" by the section or by its individual members? We would waive all precedent, all by-law requirements, and suggest that the first item of business at the important meeting of the Council on December 14, 1918, be reports from the Councilors of the number of orphans "adopted."

Six "adoptions" by members of the Society have already been recorded. May the number increase tenfold within the month!

What do we not owe to France, who for four years stood at the gateway of civilization and with all her resources, human and material, kept back the marauder? Silent in her great losses and suffering, cheerful in even the gloomiest days, determined in every fiber of her national being, she stands triumphant at last. Problems of reconstruction now confront her, and in at least one of these, the care of her orphans, it is our great privilege to share. Perhaps the little Jeans and Maries of to-day may prove to be the ties of strength which will bind France and America in closer union than could be possible through diplomatic scroll or statesmen's strivings.

#### AN EXPERIMENT IN PUBLICITY

Another experiment in chemistry has been in progress, and the results are indeed interesting.

At the April 1918 meeting the Directors of the Society appropriated \$2500 for a revival and continuance of publicity work during this year. Admittedly this appropriation was in the nature of an experiment, undertaken because of the belief that a more sympathetic bond should be established between

the public-at-large and the chemists. It was felt that this purpose could be served best by seeking to develop in each Local Section talent for popular presentation of chemical facts. Contributions of short articles were therefore asked of the members, and a payment of \$5.00 was offered for each article accepted.

The results of the experiment have just been compiled for the Directors. These show, first, that the administration and mechanical carrying on of the work is a much less formidable undertaking than was originally supposed, hence funds for continuance of this part of the work can be largely curtailed next year. Fifty bulletins have been issued to date. Returns from the clipping bureau, necessarily incomplete, show that the bulletins were used in varying numbers by 120 newspapers and magazines distributed through 72 cities in 26 states. Nineteen of the fifty bulletins were contributed by members of Local Sections other than the members of the General Committee or its office staff. All of the nineteen were received after July 30, 1918, and most of them originated within the Minnesota Section, not, we believe, because that Section has any special monopoly on popular writing but because it took hold of the matter in a live way and put some real punch into the effort. This is best illustrated by the following extracts from an announcement sent out in mimeograph form to each member of the Section:

#### Does \$5.00 look good to you?

Now that you are interested we will tell you how you can make that much money in less than 30 minutes. You are a chemist; you have a chemical hobby; you think it is really the only phase of chemistry worth working at; you feel sorry for others because they can't see all of the interesting phases of your work; you are even in a line of work which is of great scientific and practical value to the nation.

Sit down and write a 500-word article full of interest with lots of "news punch" about your favorite line of science and write it so that people may not only be interested but that they may also gain some information as to the importance of chemistry in its relation to the every-day things of life.

Send this article to Chairman Publicity Committee, AMERICAN CHEMICAL SOCIETY, 35 East 41st St., New York City. If the article is of general interest and is accepted you will receive \$5.00 in the return mail.

If you don't need the money, write an article anyhow and buy Thrift Stamps with the proceeds.

We are asked by the Society officers to do all that we can to bring chemistry home to the people. Pay your annual dues by writing two articles of general interest. The Chairman of the Committee on Publicity has requested that we bring this to your attention. Individuals and local sections will re-ceive credit for accepted articles. These articles will be pub-lished all over the country. If you have chemical items of local interest, don't fail to write them up.

If each Local Section in preparation for the new year would follow the worthy example of the Minnesota Section in presenting this matter directly to each member, we are confident that headquarters would be overwhelmed with material for consideration, and that results of incalculable value would be secured, whether or not the contributions were accepted.

Try your hand, who knows?

#### AN EMBARGO ON RESEARCH WORK

We print here a letter which has been received from a research chemist whose amiable disposition precludes his being classified as a chronic kicker:

I think the following letter from a manufacturer may interest you, as it indicates what amounts to a government embargo, in all probability unintentional, on research work in chemistry in the United States.

"We cannot ship you any phosgene for the reason that the Government has put in new regulations regarding shipments of phosgene gas.

The new regulations provide that this must be shipped in special trains accompanied by messenger. Hence you can see the impossibility of our making shipment.

I deem it imperative that this restriction on the transport of all chemicals, at least as far as universities and the chemical industry are concerned, be removed at the earliest possible date, and I trust your Journal will consider this question of sufficient importance to give publicity to the law herewith concerned, and will also suggest whatever remedy the situation may warrant. Furthermore, I am certain chemists will be interested in know-ing just what chemicals come under this embargo. I know that metallic sodium, as well as phosgene, is under the ban. Now how far can the organic chemist go without sodium? If we consider its use in the manufacture of veronal, luminal, adalim, and phenyl ethyl alcohol, substances for which there is a great demand and a limited supply, I think the predicament of the research chemists in this country, who may be engaged in de-veloping methods for the manufacture of these important pharmaceuticals, is sufficiently emphasized. We are progressing with giant strides in building up chemical industries in the United States, but we should not lose sight of the fact that the only solid foundation on which successfully to rear a permanent business in this direction is research.

Before the war there was a way to get any chemical from Germany to our laboratories. It is true there were certain rules that had to be observed in reference to containers, but the important fact is there was a "way" to get phosgene, metallic sodium, picric acid, etc. The question arises, would it not be a happy solution of the problem in hand for the Government to call to its assistance a few representative chemists and have them indicate how the needs for chemicals of every description which our laboratories and industrial plants require may be met? All the chemicals at present under embargo, with the proper safeguards, have been in the past, and could be now, transported without extra hazard.

It may be interesting to call attention to the fact that, if I am correctly informed, the only practical way for the manufacturer to obtain metallic sodium is to incur the expense of an auto truck to and from Niagara Falls.

The point raised is one which will affect every research laboratory. With the early return to the universities from war service of professors and graduate students, general research should soon get under full swing, but this important work will be sorely handicapped if a change from conditions here depicted is not quickly obtained. It is therefore earnestly urged that the proper officials of the Railroad Administration modify existing regulations so as to give the necessary relief.

#### THE RETURN OF THE CHEMISTS

In the development of the Chemical Warfare Service into an effective war machine invaluable service was rendered by Major Allen Rogers, chief of the Industrial Relations Branch, in establishing a sensible balance between the supply of chemists for service in the military ranks and in essential industries. Now that the demobilization of this great force of soldier chemists is about to begin, it is fortunate that the work is to remain in charge of the same efficient officer, as noted from the following announcement:

When the United States entered the European War one of the first problems to be considered was the effect of the draft upon our essential industries. It was early appreciated that in order to maintain our full efficiency it would be necessary to conserve

as far as possible our skilled workers and men with technical training. In order that we might not suffer from the depletion of our ranks, steps were taken to secure deferred classification, and later on provision was made to furlough back to industry. This arrangement made it possible for chemical industries to maintain their efficiency and has contributed largely to the effectiveness of our forces in the field.

Up to the time of cessation of hostilities the Industrial Relations Branch of the Chemical Warfare Service had recommended for deferred classification 641 chemists and skilled workers. These recommendations were favorably considered, as a rule, by the Local Boards, and as a result about 90 per cent of the men so recommended were put in a deferred class.

Many cases, however, were not brought to the attention of this branch until the men had actually been called into service. Such chemists or skilled workers as were essential to industry were then furloughed in order that the production of war materials might not be retarded. Through this method 156 men had been returned to industry, and at the time of the signing of the armistice 120 more cases were pending in the Adjutant General's Office.

As hostilities cease we naturally must again turn to peace time conditions and look forward to the future development of chemical industry in America. The problem now before the Industrial Relations Branch of the Chemical Warfare Service is to assist chemists in service to secure positions where their training and experience can be used to the best interests of the Government. This enormous readjustment is rendered possible through the information gathered by Dr. Charles L. Parsons, secretary of the AMERICAN CHEMICAL SOCIETY, and through the questionnaires sent out by Major F. E. Breithut of the Personnel Division of the Chemical Warfare Service.

In order to accomplish results the chemists now in military service who desire to return to chemical industry are being requested to inform the chief of the Industrial Relations Branch concerning their future prospects, while the manufacturers are being asked to designate their requirements for chemists. The administration of this work will be carried out by the Industrial Relations Branch. Any information desired may be obtained by writing to Major Allen Rogers, Chief, Industrial Relations Branch, Chemical Warfare Service, 7th and B Streets, N. W., Washington, D. C.

Here is a definite problem of readjustment of the utmost importance, and we congratulate the Chemical Warfare Service on the promptness with which it has moved. We are led, however, to wonder what plans are being made for the demobilization of the large number of chemists secured recently for war purposes in other branches of the government service, for example, the Ordnance Department. Up to the present time we have not heard that specific steps have been taken, although the problem is fully as important in these other departments.

# AN INSTITUTE FOR COOPERATIVE RESEARCH AS AN AID TO THE AMERICAN DRUG INDUSTRY

Addresses delivered before the New York Section of the AMERICAN CHEMICAL SOCIETY, November 8, 1918

At the meeting of the New York Section of the AMERICAN CHEMICAL SOCIETY on November 8, 1918, a symposium was held upon the subject of an institute for cooperative research by chemists, biologists, and manufacturers as an aid to the development of the American drug industry. The basis of the discussion was an editorial in the September 1918 issue of THIS JOURNAL entitled "War Chemistry in the Alleviation of Suffering." At the conclusion of the regular program Dr. E. R. Weidlein, Acting-Director of the Mellon Institute, upon invitation, spoke of the early steps in the foundation of that institution. He traced its continuing growth, outlined the conservative principles which had proved such wise safeguards for its well-being, and in a spirit of enthusiastic support of the movement offered to aid to the fullest extent desired in the formulation of the policies of the proposed institute. In the following report of the meeting there is included a communication subsequently received from Dr. Weidlein.

As the matter under discussion was of national rather than of local import, the resolutions adopted at the close of the meeting were referred to the Advisory Committee of the AMERICAN CHEMICAL SOCIETY.

The feeling of those present at the meeting seemed to be epitomized in the remark of a prominent manufacturer who said, "Something has been started to-night."-EDITOR.

#### A NATIONAL INSTITUTE FOR DRUG RESEARCH

By JOHN J. ABEL

I am greatly interested in the plan for a national institute in which chemists would coöperate with specialists in the medical sciences to produce new remedies for the alleviation of human suffering.

The need for such an institute is very great and its opportunities are boundless.

Among the many problems which it might undertake would be the isolation of powerful drug principles, like the so-called hormones, problems which cannot be solved without the help of the funds and the facilitics offered by a great central institute. For example, the investigator who attempts to isolate the active principle of the pituitary gland, the most powerful uterine stimulant known to medicine, finds that the price of the raw glands is six dollars a pound in the Chicago slaughter houses and that he must be on hand with the proper equipment to work up the fresh glands as they are gathered. Considering the large amount of material necessary and the cost of all the operations involved, it is plain that the individual investigator would have no chance to solve a problem of this sort without generous financial assistance.

This is but an example of the innumerable problems, all of the greatest scientific and practical importance, that lie all about us. There are a great number of crude drugs known to barbarous, as well as civilized peoples, which should be exhaustively studied in the interest of both science and medical practice. Furthermore, with the knowledge that is already at hand, the joint labor of pharmacologists and organic chemists should lead to the synthetic production of a very great number of drugs of the most diverse qualities and remedial powers and hence of the greatest service to mankind, or, stated more precisely, combining the chemo-therapeutic data already in hand with the innumerable hints that are given by nature's own remedies should yield an enormous return in new synthetic products.

The time at my disposal does not permit me to elaborate this theme as much as I could wish or to cite examples in illustration. The wonderful work of Ehrlich in giving us organic arsenical derivatives for the cure of syphilis is an illustration of what was accomplished by the combined labors of pharmacologists and chemists supported by adequate funds. What has been done in our own country in the way of the isolating of active principles from natural sources, as well as in the production of synthetics, should make us certain that from the large number of trained pharmacologists and organic chemists among us a group of men could be selected who would turn out brilliant work in a national institute such as has been proposed.

What are the requirements for a successful national institute of therapeutics and pharmacology, or whatever it might be called?

I—A large endowment, the income of which should be sufficient to finance the following groups of workers.

II—Workers: Group I would consist of pharmacologists who should have some knowledge of chemistry as well as of medicine. With this group must be associated a certain number of pathologists, bacteriologists, biological chemists, and such other specialists from the medical and biochemical field as the needs of the work require, a fluctuating number, at least in subordinate capacities. Biological, chemistry, however, would play such a large rôle that this first group would always contain at least one eminent leader in this field.

This first group would in the course of time naturally divide itself into various sub-groups each devoting its energies to a special field, but all working in close coöperation. Thus, it is evident that there would be a sub-department for pharmacological and toxicological testing of new drugs and poisons. Such a sub-department could very easily train young men to take positions with manufacturing firms which more and more require the service of such men. This department of the institute could also undertake the pharmacological and toxicological testing for individuals and firms who have no laboratories of their own.

Group 2 must be made up of capable and highly trained organic chemists and their main work would be in perfecting various syntheses, the hints for which would probably be derived from the work of the first group. Individuals of the two groups would naturally pair off to work together on some given problem.

In this second group there would also develop various subdivisions; thus, one or more men would take charge of the microchemical and ultimate analysis. In time there might even be a division for the prosecution of pharmaceutical chemical research; a subdivision of this character could be depended on to stimulate scientific pharmacy in this country.

I will not now elaborate further on the various sub-

divisions of a national institute of the character under discussion. I would, however, emphasize that the two important things to be borne in mind are:

(1) A sufficient endowment to make the institute independent of any outside influences.

(2) The Board of Trustees of this institute must see to it that those selected for the leading positions are men of ability and promise, whose one interest is research of a high order, whether in the field of pure or of applied science.

It is evident that an institute of this kind must do work in both pure and applied science as indicated in the above outline.

While I have attempted to give a brief outline of what seems to me a feasible scheme for the development of our proposed institute, I would welcome any modification, however extensive, which would be found advisable by those selected to man such an institute, for we shall all agree that these men must be the very best that the country can furnish. Men of this caliber must be given great freedom of action.

JOHNS HOPKINS UNIVERSITY MEDICAL SCHOOL

BALTIMORE, MARYLAND

#### AN INSTITUTE OF CHEMOTHERAPY By P. A. Levene

The thought that the American chemical industry, in order to be successful and impregnable against foreign competition, needs the most careful utilization of all intermediary products, is not novel and requires no new advocates. It is also well recognized that the most profitable utilization of the intermediary products of chemical industry lies in their conversion into drugs. The problem which confronts us to-day is how to establish the American drug industry on a solid basis.

It is needless to say that in order that the production of a drug shall be profitable to American industry the drug must be American in origin, and in order to be successful it must equal and, if possible, excel the corresponding drugs of foreign origin.

Naturally, as in every other enterprise, one must have a certain faith that the work has promise of success. Fortunately every one of the more successful remedies is far from the state of perfection, and new fields of application of chemical remedies in connection with preservation of health or with treatment of disease are being discovered every day.

Thus the chemical knowledge of the cardiac vasoactive remedies is in an elementary state; the field of anesthetics, though it has received some attention, remains rich in promise of fruitful results; there is much to be discovered in the field of antiseptics; the chemical treatment of infectious disease is a field all new and most attractive to the chemist; and those substances known as accessory food elements or vitamines, have as yet not emerged from the darkness of mystery.

However, several conditions have to be met in order that the enterprise may end in success:

First, the existence of a chemical industry furnishing the intermediary products.

Second, the existence of facilities and equipment for pure scientific research in the field of medical chemistry.

Third, the existence of trained specialists for the required work, and finally, the existence of ample and generous material support of the work and of the workers.

The chemical industry has come to stay in this country, hence one of the conditions is already met. The question of capital is not the domain in which the biochemist is at home. I shall dwell principally on the plan of organization which will aim to satisfy the two remaining conditions.

Every one intimately familiar with the development of medicinal remedies realizes the fact that there are very few, if any, individual workers who possess all the technical skill and the theoretical information required for the development of any one remedy. As a rule, drugs are poisons. Both their toxic and therapeutic properties may be altered by the mode of administration or by chemical modifications. The rules which govern the toxicity or therapeutic properties of drugs are not constant, hence before any remedy is offered to the profession, all its toxicological, physiological, therapeutic, as well as chemical properties, have to be established. For the efficiency and expediency of the work it is most desirable that all the work should be done in close cooperation with a group of specialists, preferably housed in the same institution.

I therefore suggest the organization of an institute of chemotherapy in the broader sense of the term. The aim of the institute should be on one hand to promote this branch of science, on the other to offer the facilities to industrial institutions to solve specific problems which they may encounter.

To meet this double function the institute is to consist first, of a permanent staff of investigators engaged in free, independent, and undisturbed research; and second, of groups of workers employed by their individual industries for special investigations. The aim of the first group will be principally to advance theoretical knowledge, which ultimately may establish the correlation between chemical structure and biological action, and furthermore, to train younger investigators.

The second group shall consist of temporary units employed by the industrial institutions, but working under supervision or control of members of the permanent staff. These temporary units may then serve as a nucleus for development of laboratories housed in the respective industrial institutions.

This plan is offered as one of three possible alternatives, the other two being the coöperation of the existing industrial laboratories with either the medical college or with the government laboratories.

In order to appreciate my objection to the medical school it is necessary to recall the history of modern medicine. Medicine of to-day became a science with the development of the microscope and galvanometer. Cellular pathology, electrophysiology, and bacteriology are the foundations of recent medicine. These subjects dominate the horizon of the medical school. It is perhaps right that it should be so. True, those of us who are chemists are inclined to think that the chemical mode of reasoning will some day acquire ascendency in the medical mind, but this is a dream of the future. For the present, in the majority of medical schools, with few exceptions, the teachers and students think in terms of cellular pathology or electropotentials. This mode of thinking is scarcely conducive to the development and stimulation of chemical visions. There are other arguments against coöperation with the colleges, but time does not permit to analyze them all.

Against the coöperation with the government bureaus I have no argument of principle. I feel, however, that the existing Bureau of Chemistry is already so overtaxed with a multiplicity of functions that it can scarcely be expected to do justice to all. Besides, it is a difficult and unpromising task to educate a government to a more generous and liberal treatment of the scientist.

ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH NEW YORK CITY

#### DRUG RESEARCH AND THE BUREAU OF CHEMISTRY Abstract of Address by C. L. Alsberg

Dr. C. L. Alsberg, chief of the Bureau of Chemistry, United States Department of Agriculture, spoke extemporaneously of his deep interest in the subject of the evening, as for many years he has been particularly interested in the development of the synthetic pharmaceutical industry in the United States. In his own Bureau work along related lines has been undertaken, for the benefit of agriculture, in the production of insecticides and fungicides. The work of the Bureau's color laboratory was described and the hope expressed that with this work well established its next development would be in the closely related field of synthetic medicinals.

Dr. Alsberg agreed with previous speakers that part of the work contemplated in the subject of the evening could not be carried on under government auspices, as he felt that the federal laboratories could not be utilized for the study of specific problems for the benefit of individual manufacturers. He was confident, however, that the work of his Bureau would dovetail into the work of the proposed institute, and expressed his best wishes for the success of the movement which had within it many possibilities of lasting blessings.

BUREAU OF CHEMISTRY WASHINGTON, D. C.

#### AN INSTITUTE FOR RESEARCH IN SYNTHETIC ORGANIC CHEMISTRY

#### By A. S. LOEVENHART

In my work at the American University Experiment Station I have seen how satisfactory and effective research work in close coöperation between chemists and pharmacologists may be. The object toward which we are working there is the development of materials destructive of life, but the thought naturally presents itself that if this coöperative work is so effective in war time for the development of offense weapons, in peace time such cooperation would be of enormous value in promoting the security of life and its comforts.

I may briefly recount the way in which the work at American University has been conducted. Most of the materials are produced by chemists working in the Station. Formal conferences are held twice a week between pharmacologists and chemists, and there are informal conferences each day. At these conferences it is decided what substances should be prepared. When the materials are synthesized they are turned over to the Pharmacological Section for every sort of test. The results of these tests are then made known to the chemists and the possibilities of improving the materials are then discussed. I may say that the work has been eminently successful from every standpoint, and that the coöperation has been delightful. One can hardly realize until he has experienced it how the pharmacologist and chemist working together mutually stimulate one another.

I am therefore prepared to testify that coöperation of the kind proposed is not only practicable, but is the ideal condition for productive research. The question then presents itself: What should be the character of the proposed institution? What fundamental ideas should guide in its organization? The previous speakers have mentioned several possibilities. I propose to bring up for discussion a somewhat different type of institution. The proposition under consideration has interested me for many years, and I have only been awaiting the time when a realization of this dream might be possible. This is the propitious time for establishing such an institute, at the close of the great war, when we must face the great reconstruction period. Bold ideas, and large development along chemical lines are in order. The marvelous struggle that Germany has been able to put up against . the rest of the world has to be attributed largely to her fostering of synthetic organic chemistry, during the last fifty years, so that they have been able to develop every manner of substitute for essential things. The great war has brought home to every one the thought that national security rests largely upon chemical development and especially upon the fostering of synthetic organic chemistry. Since the fostering of this subject is essential for national security, every patriot must do what he can to see that the subject is developed so that our country shall not only be independent of the rest of the world but that it shall lead if possible in this line of work. Such organizations as the National Security League should have brought to their attention in the most forcible manner possible the essential character of organic chemistry, in order that they may not devote their entire energies to the building up of an army and navy, but may apply some effort to the more subtle and less obvious forces required for the national security, and which also in time of peace shall be a source of great value and profit to the world at large.

The question then naturally presents itself: How may the production of organic chemicals be built up into

a great industry in this country? In this connection we may for a moment consider what factors have played a rôle in Germany in building up their immense development in this field of endeavor. While the establishment of such an institute will be a wonderful stimulus and factor, it alone will not suffice. It is obvious that one of the most important factors will be the filling of our chairs of organic chemistry in the universities with the truly inspirational type of teacher, and provision must be made that he shall receive more for his service than the niggardly salaries which the universities at present pay. I understand that when the University of Heidelberg desired to obtain the services of Victor Meyer as professor of chemistry they asked him under what conditions he would come. He stated that he would require a salary of 25,000 marks; that a new chemical laboratory should be built in addition to the old one of Bunsen; and that his first assistant should be a full professor. In Germany the professor receives in addition to his salary the fees of his students, which in the case of Victor Meyer probably amounted to 75,000 marks a year. On the supposition that this story, which I have from one of Victor Meyer's old students, is correct, Victor Meyer was receiving upwards of 100,000 marks a year, in addition to whatever income he may have received from his patents. It must be borne in mind that this occurred about thirty years ago, when the purchasing power of the mark approximated that of the dollar. This story is told merely to indicate that when the German university desired to have a man to fill the chair of chemistry the authorities ascertained under what conditions he would come and met his conditions. Teachers of this type should not be allowed to go into the industries in order to receive the compensation which their talents justify.

The lack of coöperation which has existed between men in university chairs and manufacturing concerns has been due to many factors. The university man had to feel absolutely certain that his name and university connection would not be used in any way for advertising purposes. Again, many of our best drug firms have been in the habit of making unwarranted statements in their advertising which were not borne out by the facts. The drug firms, like other commercial enterprises in this country, spent far more money and laid more stress on their advertising and salesmanship departments than on research to insure that they had a product which would stand on its own merit and which would require less advertising and not such a high order of salesmanship in order to place it on the market successfully. The recent campaign for honest advertising in all lines has produced splendid effects, and the work of the American Medical Association through the Council on Pharmacy and Chemistry and the issuing of New and Non-Official Remedies has done a wonderful service which cannot be praised too highly.

The need for an institution of the type proposed is obvious when one realizes that there is no institution in America to-day where the therapeutic value of a

### Dec., 1918 THE JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY

drug can be determined in a manner acceptable alike to scientific men and physicians. To my mind such an institute should not only foster the production and testing of remedial agents, but every phase of synthetic organic chemistry should be considered within its domain. This is necessary because remedial agents may be found among any group of organic chemical products. Remedial substances do not fall entirely within the field of the coal-tar series, as many chemists seem to think.

I will briefly and roughly outline what I think should be the scope of the proposed institute. In the first place, it must be endowed. The initial endowment should be at least \$1,000,000, but preferably not less than \$5,000,000. The institute should be entirely independent of any existing institution, but it should establish very close working relations and coöperation,. especially with the following institutions: the AMERI-CAN CHEMICAL SOCIETY, the American Medical Association, the American Pharmaceutical Association, the Hygienic Laboratory of the Marine Hospital Service, the Bureau of Chemistry of the Department of Agriculture, the Chemical Warfare Service of the War Department (in case this is continued in peace times), all university departments of chemistry, research chemical institutions and industrial concerns.

There should be many departments, all headed by men of the highest rank who have the full confidence of the scientific and medical men of the country. The institute should not only encourage organic chemistry within its own walls, but in all universities and industrial concerns. To this end it should maintain the largest possible collection of organic chemicals, which would be furnished to any university or industrial concern at cost in smaller quantities. It should also be willing to synthesize for chemists any substances which they require for their work, these substances to be furnished at cost. This idea is prompted by the tremendous advantage German chemists have had in securing from industrial concerns any substances which they require in their work in almost any quantities, whereas this has been denied the best American investigators.

Another important function of the institute should be the obtaining and administering of patents by organic chemists. Any scientific man should be able to turn over to the institute any patent relating to synthetic organic chemistry on the basis that he receive as a maximum fifty per cent of the profits, or any less amount that he may elect, the remainder of the profits being his contribution to the research fund or the general fund of the institute. This would ultimately result in an institute of great financial strength, which is a matter of great importance. The institute might handle its patents by licensing a limited number of concerns to use them, or in special cases it might itself manufacture, in case existing manufacturers hesitated to make use of a given patent.

One of the departments of this institute should be devoted to pharmacology and toxicology, and it would be necessary in order to make the final therapeutic tests acceptable to the medical profession to control a hospital devoted to experimental therapy, to which only selected types of cases would be admitted. This feature alone would indicate the necessity of the institutes becoming financially strong in order to bear the expense of such a hospital.

In conclusion, I may say that I am willing and glad to do anything in my power to further such a project as this, because I have the feeling that it is a matter of the utmost importance, not only for the security of our national life but for the benefit of the world at large.

American University Experiment Station Washington, D. C.

#### AN INSTITUTE OF THERAPO-CHEMICAL RESEARCH By FRANK R. ELDRED

In an editorial in the September issue of the Journal of Industrial and Engineering Chemistry, under the title "War Chemistry in the Alleviation of Suffering," Dr. Chas. H. Herty points out the need for a research institute for the pharmacological and clinical testing of medicinal substances.

In discussing such an institute from the standpoint of the manufacturer of medicinal products, I shall not attempt to dwell at length upon its relations with the manufacturer, since successful cooperation would depend entirely upon the organization and policy of the institute and the character of the work done.

If an institute of this kind is to attain a high degree of usefulness, its organization and management, both administrative and scientific, must receive the most careful consideration. Its field of work should be distinct from that of other similar institutions already established. It is of prime importance that the proposed institute be essentially a chemical institute. It should be organized and conducted under the sponsorship of the AMERICAN CHEMICAL SOCIETY and should in some manner be closely affiliated with that organization. Upon the above propositions will rest the success of the undertaking.

During the past four years we have made wonderful strides in all branches of chemical industry and with the coming of peace, steps must be taken to make these achievements permanent assets to our country and to assure continued progress.

In the branch of chemical industry devoted to the alleviation of human suffering the proposed institute would thus have a twofold function: to aid in making us as far as possible independent of all other countries in the production of necessary and valuable medicinal products, and to encourage, as well as take an active part in, researches directed towards the discovery of more effective agents for the prevention and cure of disease. Of these two functions the latter is undoubtedly the more important. With proper governmental protection the manufacturer can be trusted to make this country independent in the production of medicinal chemicals which have an established use, but it is in the development of new medicinal agents that the great difficulties and great opportunities lie.

It should be made clear that the need is not for

more drugs but for better—and fewer—drugs. It would be of slight value to establish an institution merely for the purpose of testing, pharmacologically and clinically, new or old drugs which might be submitted to it, but it would be difficult to estimate the immense value of a great research center for the study and improvement of our present chemical agencies for combating disease. In the ultimate analysis all agencies for this purpose are chemical agencies, just as the life processes are chemical processes, and it is for this reason that the institute should be so organized and supervised that all of the problems which come to it will be attacked from the chemical standpoint.

It is a rather disquieting thought that we know almost nothing about the mechanism of the action of medicines and that our present medicines have been developed by empirical methods. The effects of many drugs now widely used were discovered accidentally, while certain synthetic drugs were apparently developed for the purpose of utilizing a cheap byproduct or a readily available intermediate, and still others were discovered by trying, more or less indiscriminately, one substance after another until one was found which had the desired action. Only a few of the many German synthetic drugs have proved to be of real value, while the larger number have been foisted upon the public by clever propaganda. It is not desirable that an institution should be established to foster this kind of research. Probably no one but a drug manufacturer knows how many remedies are proposed by chemists and others not chiefly occupied in the development or production of medicinal substances and therefore without any broad knowledge of the needs of medicine. No excuse can be found for many such proposals; some are based upon unsound reasoning and others are entirely lacking in originality, frequently to the extent of having been previously tried and discredited. It would only increase the number of drugs and at the same time lower their average efficacy if drugs inferior to those already available were placed upon the market. A research institute such as we are considering must not therefore lend its influence to the multiplication of drugs of doubtful value nor waste time in the investigation of many of the remedies which might be proposed.

Although little is known in regard to the manner in which medicines produce their physiological effects, animal experimentation and clinical tests have yielded a great mass of facts in regard to the effects which are produced by various drugs and this forms the foundation of our present efforts in the development of remedial substances. Such facts are of course very important and must not be disregarded. As a result of such studies it has been possible to correlate molecular structure with physiological action in such a way that it has become a most valuable guide to the chemist working in this field, but when substances of such diverse constitution as cocaine, guinine, novocain, benzyl alcohol, and magnesium salts all act as local anesthetics, it becomes apparent that we must look more deeply for the cause of their physiological action.

The problem is one for the physical chemist, and until the methods of physical chemistry are applied to the study of drugs and the actual mechanism of their action is investigated, we cannot hope for real progress in this most important field. Pharmacology, the study of the action of drugs, then becomes a study involving the application of recognized physical and chemical laws to the investigation of the reactions occurring between the living organism and the chemical agents employed. It is along such lines that an institute of pharmacology or therapo-chemistry should be developed rather than along the more superficial lines usually thought of in connection with pharmacological work.

It is evident that animal experimentation of the conventional type is necessary in order to establish the action and value of drugs and that connections with hospitals of the highest class must be maintained so that clinical trials can be carried out under the most favorable conditions, but this part of the work, while indispensable, should be subordinated to the fundamental researches already mentioned.

If an institute were organized in which fellowships could be established by manufacturers or others for the study of specific problems, the usefulness of the institute would largely depend upon the support which the institution received in this way as shown by the number of fellowships maintained. It is safe to say that an institute of the character which has been outlined, under the management of men having the proper conception of the work and the necessary training and experience for directing it in an efficient manner, would receive the support of the manufacturers. It would of course be necessary to guarantee to those establishing fellowships, advance reports of the work and proper patent protection. This would give the manufacturer without research facilities an opportunity to secure the advantages of research of the highest type and at the same time to contribute something to the sum of knowledge in the field from which all or part of his livelihood is derived. The manufacturer with research facilities would often welcome an opportunity to supplement the work carried on in his own laboratories by establishing fellowships in a wellequipped and competently supervised institute.

If this branch of the chemical industry is built up in this country along the lines indicated, it will add to our national prosperity and at the same time contribute to the welfare of mankind. To bring about this result the manufacturer must receive the support and protection which will enable him to make his business profitable. It must be remembered that with the exception of a very few drugs which have come into general use by the laity, the volume of sales of any one medicinal substance is very small when compared with the relatively enormous sales of many technical chemicals and other manufactured commodities. The responsibilities and almost endless detail entailed in this branch of manufacturing are also out of all proportion to the returns. The commercial possibilities are therefore not sufficient to justify expensive research and the installation of costly manu-

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facturing equipment unless the manufacturer can secure, for a limited time, a monopoly in the sale of the products which he originates. Indeed it often happens that on account of the limited demand for many well-known medicinal chemicals their manufacture cannot be made profitable if engaged in by more than one manufacturer. The drug manufacturer must therefore receive the full measure of protection accorded to other manufacturers. He must not be discriminated against in the matter of patent protection as has been advocated in certain quarters. No other factor could be more potent in preventing progress in this branch of industry than the elimination of product claims from chemical patents. Since the progress of the industry depends upon the success of the manufacturers engaged in it, one of the most important duties of the institute would be to assist the manufacturer of medicinal products in every way consistent with the objects to be accomplished.

An institute organized for the purpose of promoting the welfare of the industry and at the same time the health and welfare of the people, and conducted along the most strictly scientific lines could not fail to have a far-reaching influence. It would be a unique institution of which the founder, the AMERICAN CHEMICAL SOCIETY, and the Nation could be justly proud.

Dr. Herty deserves great credit for discerning the need for such an institution and for laboring so unselfishly to make it a reality.

ELI LILLY AND COMPANY INDIANAPOLIS, INDIANA

#### INSTITUTE FOR RESEARCH ON SYNTHETIC DRUGS By D. W. JAYNE

My contribution to this subject is an endeavor to give the viewpoint of the manufacturer of synthetic drugs, or the manufacturer who could, under certain conditions, properly become a producer of these drugs.

There is no doubt that the field of synthetic drugs, especially of a coal-tar origin, has been largely overlooked by American chemical manufacturers. Many concerns have entered the manufacture of dyestuffs, and that industry has, no doubt, come to stay, but many of the dyes that are still lacking are those of comparatively small tonnage. It is the tonnage of an article that usually first attracts the American manufacturer, and synthetic drugs cannot be considered from a tonnage standpoint. With the coming of competition on the items of larger tonnage the products used in smaller quantities are turned to, and have frequently been found to be more remunerative than the larger volume items.

The coal-tar drugs which are made here to-day, are, like the dyes, merely copies of those formerly imported from Germany. With the coming of competition on the old lines in the dyestuffs, the manufacturers are putting more and more effort on research work to discover new dyes, and it is a safe prediction that the results of our American chemists' work in research on dyes, will lead to new things in that field.

It is also safe to believe that if American chemists begin in earnest on research in drugs, surprising results will be obtained. The field is certainly broad enough to give ample opportunities to satisfy both the pure scientist and the investor.

This turning to the coal-tar and other synthetic drugs by present chemical manufacturers, especially of dyestuffs, is certain to come. Peace time uses for the vast resources of this country developed for war purposes are sure to be sought. This field, however, can be pressed forward to the attention of manufacturers, and it should be.

I express, I believe, the thought of our Chairman, when I say it is right and proper that the forces which wrought for destruction in war time, should, in peace time, turn to the conservation of the health and happiness of the human race.

The great obstacle to the development of the synthetic drug industry from the manufacturer's point of view is, in my opinion, the inability to properly try out the results obtained in the laboratory. In research on dyestuffs, a new product or an old one can be definitely tested in the manner of its intended use, but lacking any constructive theory, the application of the results of the research chemist in drugs can be determined only in an unsatisfactory way at present.

I am, therefore, of the opinion that the establishment of such an institute as we are discussing, if properly carried out, would be the greatest stimulus to the rapid creation and development of a real American synthetic drug industry.

I believe that this institute should have two functions: First, research in the pure science, to determine the general effects on the human system of each class of chemical compounds, and the probable relative efficiency of these compounds by classes against certain ailments; second, the determination of the efficiency for the purpose proposed of any drug submitted to it by a manufacturer, with a simultaneous determination of any side- or after-effects of the use of such drugs.

Under the first head would come, for example, the determination as to whether the introduction of the acetic acid radical tends to increase the febricidal efficiency of given compounds, and how that increase in efficiency compares with the introduction of, say, a formic acid radical.

Under the second heading would come the submission of a drug, claimed, for example, to be more efficient than salvarsan. This would require considerable work, not only to determine its efficiency as a specific, but to establish the quantities to be used over a given period to secure results without consequent side effects. This would imply that the determination of the proper dose should be a part of such investigations.

Both of these functions would require the highest integrity and ability in the institute as an organization, and in its personnel individually. Its work in pure research should be recognized as the best authority. The results of such research would then make more evident to the chemists in the industry the direction in which to make their effort, either in finding a drug for a specific purpose, or finding a purpose for a drug which would be especially fitted for their manufacturing conditions.

The second-mentioned function, that of reference for report, also makes it essential that such an institute be conducted on the highest plane, to insure the confidence of the manufacturers and also of the medical profession, which above all must be convinced of the merits of the drugs, in order to provide a market for them not based merely on clever advertising.

I am not attempting to detail the method by which the research in the pure science should be carried on, whether by fellowships or otherwise, except that the central organization should be big enough and strong enough to pass on any work done, and approve or disapprove of the results in the name of the institute.

This same central organization would also necessarily be charged with direct supervision of the work done on drugs submitted to it. The manufacturer who submitted a drug would pay for the report on it, but the institute should not submit to limitations on the work to be done. The results, of course, would belong to the manufacturer, and if the report showed lack of merit of the product, or harmful effects from its use, it would be for the information of the manufacturer, a favorable report also being his, for use with proper and necessary restrictions.

The institute could cover synthetic flavors and perfumes, as well as drugs, as, especially in the case of flavors, the absence of toxic or other harmful effect is a necessary requisite.

It is also entirely possible, even probable, that certain natural products now used in food, can be nearly duplicated synthetically, and such products would certainly be proper ones for submission to the institute.

It has also occurred to me that this same institute could fill another want, that of the investigation of industrial diseases, due to working in various chemicals. No doubt many concerns had unlooked-for trouble with occupational diseases when they began the manufacture of dyestuffs and explosives ingredients. The effects of working in nitro compounds are well recognized, but what effects should be expected in the manufacture of other and more complex compounds should be studied and made available to prospective manufacturers, as well as methods of avoiding and combating these troubles.

The effect of these various compounds on the man working in them is certainly a parallel problem to the use of certain finished products to purposely produce a result on the human system.

No doubt the results of the research of such an institute would shortly lead to an ability to definitely predict results in the manufacture or use of any given product.

#### SUMMARY'

I—Chemical manufacturers should be encouraged to enter the wide field which exists in the production of synthetic drugs.

II—To secure rapid and proper development, a ink should be formed between the manufacturers and the medical profession. III—An independent organization of the highest type of men is needed to form this link.

IV—If formed, it would undoubtedly be used by the manufacturers, and should shortly become the leading factor in the situation.

THE BARRETT COMPANY

NEW YORK CITY

#### REMARKS CONCERNING SUGGESTION FOR CENTRAL MEDICINAL RESEARCH LABORATORY

#### By E. R. WEIDLEIN

The various papers presented on the necessity for a central medicinal research laboratory were exceedingly interesting and show conclusively the need for such an organization. The matter has come to my mind several times since the meeting, and, while my few remarks were along the lines of coöperation with medicinal manufacturers, I do not believe that the importance of this cooperation was sufficiently emphasized. The industrialist needs all possible assistance in undertaking and developing research work as a means of enlarging his output and improving its quality. However, in order to be effective, this assistance must increase his independence and power of initiative and be so given as to enlist his active support. It has been the coöperation of progressive industry with science which has led to the practical application of the results obtained in the laboratories of scientific men. Fortunately the policy of industrial secrecy is now being more generally regarded in the light of reason and more liberal views are taken, thus bringing about a closer union between science and industry. Nevertheless, large corporations will not be willing to enter into such a scheme of coöperation until they have a vivid and broad comprehension of the need of the efficiency which the scheme represents and a realization that the scheme itself is founded on sane and practical considerations.

It is also equally important that the central medicinal research laboratory should have complete control over its work, and especially, over how the results shall be used. The introduction of a commercial atmosphere or the use of its results for advertising purposes would soon prove fatal to such an institution.

It is important to realize that investigations on a large scale ultimately bring considerable benefit to the community generally, that every scientific discovery applied through industry results to the public gain, and that, consequently, industrial organizations will be justified in supporting a movement to carry on such investigations, since it is only where there are large aggregations of capital that the most extensive and productive research facilities can be obtained.

The Mellon Institute of Industrial Research is willing at all times to coöperate and render any informative service necessary for the establishment and organization of such a laboratory. A spirit of coöperation should be encouraged among all types of research laboratories, as no greater good to society can arise than from a wider distribution of the duties and responsibilities of research.

Mellon Institute for Industrial Research Pittsburgh, Pa.

# CHEMICAL MARKETS OF SOUTH AMERICA

#### By O. P. HOPKINS, Washington, D. C.

### THE CHEMICAL MARKETS OF COLOMBIA, ECUADOR, THE GUIANAS, VENEZUELA, AND PARAGUAY

Received October 30, 1918 Excluding Paraguay, the countries considered in this article form the northernmost portion of the continent and all fall within the tropics. They are not so well developed as the countries treated in previous articles of this series, although like them, they have great resources awaiting outside capital and direction. The fact that they are within comparatively easy reach of American ports gives our traders an advantage that they do not possess in the countries farther south, and make the markets much more attractive than might at first thought be suspected. This is particularly true of the markets for medicines, toilet articles, paper, and so forth.

To most of these countries the war has meant increased prosperity, as their products have been in unusual demand. Capital has accumulated as the result of shipping restrictions which have cut down their imports, and it is reasonable to assume that the coming of peace will find the inhabitants with more money to spend than ever before and a pent-up desire to spend it. Trade with Colombia and Venezuela, which has always been attractive to Americans, should be even more so when normal conditions are restored. While trade with the other countries will increase, it will not be of great importance, comparatively, for many years to come.

Paraguay, which does not belong to this group of countries geographically, is nevertheless included to make the series complete. It should perhaps have been considered in the first article with Argentina, Brazil, and Uruguay.

As in the other articles, there is given for each country a table showing the imports of chemicals and allied products from all sources, compiled in each case from the official statistics of the country under consideration. These figures are in some cases meager, are never very nearly up to date, and are in some respects not particularly accurate. They should be used only as a general guide to the extent of the markets. The tables showing the trade with the United States are compiled from statistics published by the Bureau of Foreign and Domestic Commerce of the United States Department of Commerce.

#### COLOMBIA

Lack of transportation, an indifferent labor supply, and small white population have in the past retarded the development of Colombia's magnificent mineral resources, upon which depend the prosperity of the country. In recent years, however, there has been a decided change for the better, in which American capital and machinery have been prominent factors. The opening of the Panama Canal has been a great help, and since the reaction that followed the outbreak of the war the country has had its share of war prosperity. Gold is the principal product and silver is mined to some extent. As the only important source of platinum outside of Russia, the country has aroused much interest in Allied circles. Emeralds are also an important product, and there are supplies of iron, coal, salt, and petroleum, although they have received but little attention. Manufacturing and agriculture are comparatively unimportant.

Considering the size of the white population, Colombia has been a rather important purchaser of the products considered in these articles, and American houses have done the bulk of the business, although previous to the war Germany's share was not inconsiderable, as is shown in the following table, which is a compilation from the Colombian official statistics for the latest available calendar year.

COLOMBIAN IMPORTS OF CHEMICAL	S AND ALLIED	PRODUCTS
ARTICLES	1914	1915
CHEMICALS, DRUGS, MEDICINES,		1710
DRUGGISTS' ARTICLES	\$750,123	\$797,076
France	137,890	\$191,010
Germany	134,323	
United Kingdom	87,930	
United States	325,992	
COLORS, PAINTS, INKS, VARNISHES.	118,909	150,784
Germany	33,489	
United States	62,594	
SOAPS AND PERFUMERY	112,249	87,722
· France	16,673	A CONTRACTOR OF THE OWNER
United Kingdom	21,291	
United States	65,012	
EXPLOSIVES	79,281	86,824
United Kingdom	37,835	
United States	30,940	
OILS AND FATS, EXCLUSIVE OF MIN-	A PARA MALING STREET	
ERAL OILS	194,749	180,713
United Kingdom	16,357	
United States	135,625	500 040
MINERAL OILS AND COMBUSTIBLES	540,081	590,848
Germany	43,811 57,175	
United Kingdom	344.776	
United States	344,770	
GLASS AND GLASSWARE, EARTHEN- WARE, STONEWARE	481,890	242,398
Germany	124,510	242,390
United Kingdom	95,164	
United States	180,512	
PAPER, CARDBOARD, AND MANUFAC-	100,012	
TURES OF	551,582	494,673
Germany	122,629	
United States	195,458	

That the war greatly increased the dependence upon supplies from the United States is shown in the next table, which is based upon American statistics for the fiscal years 1914 and 1917. The marked gains under the heading "Chemicals, drugs, dyes, etc.," are in a measure due to high prices, but may in part be attributed also to the fact that former European sources had been cut off and to the fact that the purchasing capacity of the country had increased. It is unfortunate that the most striking gain under this head is entered as "All other." The most impressive increase in the list is shown for paper, \$85,165 to \$688,310. Colombia is a market that deserves close attention from American exporters.

As a source of supplies for the materials under consideration in these studies, Colombia is noted chiefly for platinum, of which more than a million and a half dollars' worth was imported into the United States in 1917. Rubber and tanning extract are the only others of any importance purchased from that country. AMERICAN PRODUCTS SOLD IN COLOMBIA

AMERICAN PRODUCTS SOI	D IN COLOMBIA	
ARTICLES	1914	1917
Aluminum and manufactures	\$ 228	\$ 21,793
Babbitt metal	640	1.680
Blacking, shoe paste, etc	7,246	11,312
Celluloid and manufactures	1,221 126,333	50,003
Cement, hydraulic	126,333	122,277
Chemicals, drugs, dyes, etc.:		
Acids:	E 200	6 757
Sulfuric All other	5,328 . 3,212	6,757 32,222
Dyes and dyestuffs	. 5,212	24 372
Medicines, patent or proprietary	254,643	24,372 342,157
Petroleum jelly, etc	765	5,858
Roots, herbs, barks Soda salts and preparations	195	5,858 4,053
		65,594 540,863
All other	92,232	540,863
Explosives:	0 601	0 400
Cartridges, loaded	8,681	9,400 33,401
Dynamite Gunpowder	7,483 25,461	17,440
All other	9,218	17,440 145,255
Flavoring extracts	5,143	10,343
Glass and glassware	56,034	233,804
Glue	1,182	5,238
Grease:	T FOF	17 040
Lubricating	7,525	17,040
Soap stocks and other India-rubber manufactures	5,639 38,212	2,923 107,603 23,255
Ink	6,412	23,255
Leather, patent	9.232	33,719
Naval stores	49,457	81,112
Oilcloth and linoleum	9,232 49,457 10,345	14,443
Oils:		
Animal	74	646
Mineral:		150 014
Gas and fuel.	97,527 161	150,014 6,467
Illuminating	148,045	45,609
Lubricating, etc	67,946 33,709	38,050
Gasoline	33,709	81,047
Other light	1,184	911
Vegetable:	0. 500	F 101
Cottonseed	2,523	5,424
Linseed	6,629 4,362	33,077 20,077
All other fixed Volatile	2,263	6,656
Paints, pigments, etc.:	2,200	0,000
Dry colors	4,634	19,128
Ready-mixed paints	23,416	45,691
Varnish	4,562 789	7,319 1,636
White lead	789	1,636
Zinc oxide All other (including crayons)	6,538	6,719 54,106
Paper and manufactures	85,165	688 310
Paraffin and paraffin wax	55,750	688,310 130,259
Perfumery, cosmetics, etc	17.325	37 159
Photographic sensitized goods	7,290	14.796
Plumbago and manufactures	916	5,978
Soap:	in and the	
Toilet	28,675	44,875
All other	32,096	14,413 5,573
Stearin, vegetable	5,374	17 616
Sugar and molasses	1,350	17,616 9,188
It was and manufacture or receiver the	.,	,,

Ipecac, which grows wild, is exported to the extent of fourteen or fifteen tons annually, but no imports into the United States are shown separately in the statistics. The following table shows imports from Colombia into this country for the fiscal years 1914 and 1917:

COLOMBIAN PRODUCTS SOLD IN THE UNITED STATES

ARTICLES	1914	1917
Chemicals, drugs, dyes, etc.:		
Extracts for tanning	\$ 25,494	\$142,064
Chicle		515
Indigo		6,128 5,886
Copper India rubber, etc.:	OTI	5,000
Balata		243,322
India rubber	175,870	492,432
Oils:		
Animal.		4.650 239
Vegetable Platinum:		239
Unmanufactured	398,657	1,524,039
Ingots, bars, etc		12,383
Tanning materials, crude:	an weight and	
Mangrove bark	80	9,169
Quebracho wood		2,887
All otherZinc	300 114	5.168
2/1001111111111111111111111111111111111	111	5,105

#### ECUADOR

As Ecuador is the smallest country on the West Coast and has a white population of not much more than two hundred thousand, the market for imported goods is naturally limited, and it would be an exaggeration to say that much improvement in that respect can be expected in the near future. The mineral resources have barely been scratched, agriculture in the main has received little attention, and, aside from the Panama-hat industry, which does not require imported equipment or materials, there is very little manufacturing. Cacao beans make up more than half of the exports ordinarily, the other principal products entering the export trade being Panama hats, ivory nuts, coffee, rubber, gold, and hides, the total in normal times not amounting to much more than thirteen million dollars.

Very little in the way of chemicals is imported, but such business as there was in normal times was fairly evenly divided between the United States, France, England, and Germany, in the order named. In drugs and medicines the United States has had the advantage of all competitors. Belgium was formerly most successful in supplying the demand for soap, England has a virtual monopoly of the candle business, and Germany was favored in orders for paper, as the following official Ecuadorian figures show:

netal Dettational inguies show		
ECUADORIAN IMPORTS OF CHEMICA		
ARTICLES	1913	1915
CHEMICALS, DRUGS, MEDICINES	\$299,558	\$284,184
Drugs and medicines	139,534 26,432	195,436
France	26,432	54,331
Germany	22,814 15,265	113 11,515
United Kingdom United States	65,315	114,072
Chemicals, n. e. s <sup>1</sup>	54.776	12,132
France	17,296 8,698	1,659
Germany	8,698	
United Kingdom	10,800	119
United States	17,560 136,888	9,786 158,521
Soap, ordinary	126,016	143,338
Belgium	51,189	10,348
Germany	24,103	-97
United Kingdom	35,992	24,209
United States	4,416	53,885
Soap, perfumed	10,872	14,572
United States	9,699 34,659	13,593 33,900
PAINTS AND VARNISHES House paints	24,866	20,966
France	8,468	4,727
United States	7,070 86,960	10,742
ARMS, AMMUNITION, EXPLOSIVES	86,960	42,193
Dynamite	12,787 12,787	14,616
United States	109,230	14,616 164,003
STEARIN CANDLES AND PARAFFIN Stearin candles	106,322	151,700
United Kingdom	89,721	143,920
United States	1.625	143,920 5.741
OILS, ANIMAL AND VEGETABLE	77,901 20,830	74,400
Olive oil	20,830	25,520
Italy	14,214 4,020	17,747 6,179
Spain Machine oil	24,919	13,397
United States	16,733	12.915
OILS, MINERAL, AND COMBUSTIBLES.	330,067	327,176 56,015
Gasoline	57,768	56,015
United States	2,958	605
Kerosene, refined petroleum	72,821 71,643	76,525 75,542
United States GLASS, GLASSWARE, EARTHENWARE	99,655	41,880
Sheet glass	10,783	7,563
Belgium	2,602 .	3,179
Germany	6,645	
United States	291	3,723
PAPER AND CARDBOARD	152,400	119,968 26,458
Printing paper Belgium	47,718 7,761	20,430
Germany	78 557	3,347
United States	9,284	20,369
Writing paper	21.813	11,662
Belgium	5,227	55
United States	5,831	6,695 199,075
PERFUMERY AND TOILET ARTICLES	73,400	199,075

While the sales of American chemicals and allied products are not imposing, there has been a substantial gain all around since the war started, and as our exporters are more advantageously situated geographically than their competitors there is no reason to suppose that the increased business cannot be maintained, at least in part, when normal conditions are restored. The effect the war has had on the trade is shown by the following fiscal year American figures:

<sup>1</sup> Not elsewhere specified.

AMERICAN PRODUCTS SOL	LD IN ECUADOR	
ARTICLES	1914	1917
Aluminum and manufactures	\$ 44	
Blacking, shoe paste, etc	3,224	\$ 2,138 14,971
Candles	19	3,410
Celluloid and manufactures	632	16,849
Cement, hydraulic	9,198	59,790
Chemicals, drugs, dyes, etc.:	a state water and	server and the server
Acids	510	6,666
Copper sulfate	270	1,309
Dyes and dyestuffs	124	7,578
Medicines, patent and proprie-	00 454	
Soda salts and proparations	98,454	71,564
Soda salts and preparations All other	( <i>a</i> ) 31,082	13,588 141,877
Explosives:	51,002	141,0//
Cartridges, loaded	8,720	13,115
Dynamite	60,142	13,210
Gunpowder	4,058	30,597
All other	3,733	8,564
Glass and glassware	7,426	76,076
India-rubber manufactures	48,289	42,265
Ink	2,077	7,250
Naval stores	6,544	11,612
Oilcloth and linoleum	4,691	22,517
Refined mineral:		
Illuminating	67,855	66,660
Lubricating	19,825	21,669
Vegetable:	and the net read	and the second second
Linseed	561	5,296
All other	6,164	10,862
Paints, pigments, etc.:		No. of Concession, State of Co
Dry colors	265	7,709
Ready-mixed paints All other (including crayons)	5,878	7,314 15,923
Paper and manufactures	7,093 78,089	293,344
Paraffin and paraffin wax	321	22,026
Perfumeries, cosmetics, etc	11,802	52,917
Photographic sensitized goods	693	5,137
Soap:		
Toilet	13,103	23,516
All other	1,081	46,633
(a) Not stated separately in 1914.		

(a) Not stated separately in 1914

The next table, also based upon American returns for the fiscal years 1914 and 1917, shows that of the materials under consideration rubber alone is exported to the United States in anything like an appreciable quantity.

ECUADORIAN PRODUCTS SOLD	IN THE UNITED	STATES
ARTICLES	1914	1917
Bones, hoofs, horns Chemicals, drugs, dyes, etc.:		\$ 2,174
Extracts for tanning		2,538
All others		12,893
Copper	17,570	991
India rubber, etc.:		
Balata	ACCORD TO	3,908
India rubber	136,903	296,208
India-rubber scrap		80
Tungsten-bearing ore		5,300
DDITTOT CIT	ATA	

#### BRITISH GUIANA

Of the three Guianas, the British colony is the most important, but it does not offer an extensive market for American goods. Sugar makes up the bulk of the exports from the country, although there are some shipments of gold, rum, balata, and rice. England ordinarily furnishes about half the imports and, with Canada, takes the major portion of the exports. The imports of chemicals and allied products from the United Kingdom and the United States in 1913, 1914, and 1916 are shown in the following table, other details of origin not being available.

IMPORTS OF CHEMICALS AND AL	LIED PRODUCTS	INTO BRIT	TISH GUIANA
ARTICLES	1913	1914	1916
UNITED KINGDOM: Medicines and drugs (not containing alcohol):			
Patent and proprietary	\$ 18,877 42,402	\$ 16,959 66,317	\$ 20,440 93,641
Oils, all kinds	32,450	38,724	45,856
Soaps, all kinds Paints, colors, pigments	94,035 23,805	113,432 23,174	129,096
Paper and stationery <sup>1</sup>	53,534	59,180	87,154
Glass and glassware UNITED STATES: Medicines and drugs (not containing alcohol):	14,974	16,109	19,369
All other, and chemicals.	8,457 18,963	13,721 29,336	17,333 112,038
Oils: Petroleum, refined All other	106,551 110,787	99,494 148,647	138,819 204,001
1 Does not include printing	naper which	however	is not shown

<sup>1</sup> Does not include printing paper, which, however, is not shown elsewhere.

The next table shows that the United States has improved its share of the trade in chemicals and allied products since the war started. These are fiscal year American figures.

morroun nguros.		
AMERICAN PRODUCTS SOLD	IN BRITISH GUIANA	
ARTICLES	1914	1917
Blacking, shoe paste, etc	\$ 6,281 \$	
Candles		3,106
Cement, hydraulic	5,617	36,293
Chemicals, drugs, dyes, medicines:		,
Acids:		
Sulfuric	6,491	26,095
All other	8,303 .	25,361
Medicines, patent or proprietary	18,166	14,893
Petroleum jelly Soda salts and preparations of	1,419 (a)	1,550
All other		3,627 140,103
Explosives	3,733	2,487
Fertilizers	100	18,836
Glass and glassware	960	15,625
Grease:		and the second
Lubricating	539	3,537
All other	245	355
India rubber, manufactures of	8,940	17,689
Matches Naval Stores:	35	3,255
Tar, turpentine, pitch	4,598	5.736
All other	1,194	2,356
Oils:	Contraction of the second	2,000
Animal	1,845	3,726
Mineral:		
Fuel and gas	1,297	7,119
Gasoline	31,736	13,887
Illuminating Lubricating, etc	95,950 14,878	86,454
Vegetable:	14,070	30,281
Corn	4,769 1	02,725
Cottonseed	98,357	20,930
All other	57	2,628
Paints, pigments, colors, varnishes:	The second second second	and the second second
Ready-mixed paints	721	2,971
All other (including crayons) Paper and manufactures	1,270 .	5,615
Perfumeries, cosmetics, etc	6,417 6,701	56,986 15,703
Photographic goods	244	6,544
Salt		4,833
Soap:		.,
Toilet	2,110	5,227
All other	10	8,657
Sugar, refined	12,002	16,430
(a) Not stated separately in 1914.		
		The second second second

Sugar and balata are the only materials of the sort under consideration imported into the United States from British Guiana, as the following table, for fiscal years, shows.

PRODUCTS OF BRITISH GUIANA SOLD	IN THE	UNITED STATES
Articles	1914	1917
Clays or earths India rubber, unmanufactured:		\$ 3,577
	58,284	150,102
India rubber Sugar, cane	125	23,543 737,456

#### DUTCH GUIANA

Conditions in Dutch Guiana do not differ greatly from those in the British colony and do not promise to improve sufficiently in the near future to make the market an attractive one for chemical products. Balata is the principal product of the country, followed by

IMPORTS OF CHEMICALS AND ALLIED	PRODUCTS	INTO DUTCH	GUIANA
	TOTAL	IMPORTS	FROM
	IMPORTS	Nether-	United
ARTICLES	1913	lands	States
CHEMICALS, DRUGS, ETC.			
Acid, acetic, and vinegar	\$ 3,635	\$ 3,474	
Alcohol, ethyl	50,525	45,393	\$ 564
Alcohol, methyl	490		
Chemicals, n. e. s	33,610	20,708	6,523
Ether and chloroform	64	63	
Fertilizers	20,859	8,531	1,044
Opium	3,382	3,202	
Perfumery	7,022	5,015	1,251
			1,201
OILS, VEGETABLE Aromatic	1,240	1,000	110
Coconut, linseed, olive, rape, ma-		-,	
chine	67,601	45,990	15,651
OILS, MINERAL			,
Benzene and gasoline	4,535	1,024	2,006
Crude petroleum	1,754	19	1,727
Kerosene	44,420	2	41,954
EXPLOSIVES:			
Gunpowder	3,900	3.898	
COLORS AND PAINTS	32,318	30,544	82
VARNISHES	873	795	50
GLASS AND GLASSWARE	7,626	7,080	248
PAPER	20,570	18,211	1.864
		States of the states	

sugar, gold (which is mined in a primitive manner), and cacao. Manufacturing and agriculture are of little importance.

A glance at the preceding table will show that the market for chemical products is of little consequence and that such trade as there is, is dominated by the mother country. The statistics here given are for 1913, the latest available in the official records of the country.

The next table shows that the colony has been forced by the war to turn to the United States for supplies, but the total is, of course, not impressive even now. These figures are for fiscal years and are from American records.

AMERICAN PRODUCTS SOLD	IN DÜTCH GI	UIANA
ARTICLES	1914	1917
Blacking, shoe paste, etc Candles	\$ 368 1,291	\$ 2,914 7,019
Cement, hydraulic Chemicals, drugs, dyes, medicines:		8,225
Acid, sulfuric Copper sulfate	512 1,448	360
Medicines, patent or proprietary	5,533	6,252
All other	2,339	22,430
Glass and glassware	649 753	3,403
Grease India rubber, manufactures of	658	4,554 5,491
Oils:	000	0,101
Mineral:		0 100
Fuel and gas	4,652	8,522 12,068
Gasoline Illuminating	46,966	88,283
Lubricating, etc	3,221	12,152
Vegetable: Cottonseed	- 000	70 207
Linseed	7,989	70,397 5,010
All other	9	2,882
Paints, pigments, colors, varnishes:		
Ready-mixed paints	65	2,787
All other Paper and manufactures	281 9,312	4,366 20,426
Perfumeries, cosmetics, etc	967	2,197
Soan:		and the second second
Toilet	506	1,986
All other Sugar, refined	3,122 8,661	9,301 8,900
5464, 1000000, 100000, 1000000, 1000000, 100000000	0,001	0,000

Sugar, cacao, and balata are the only materials of any importance imported into this country from Dutch Guiana, as the following table shows.

PRODUCTS OF DUTCH GUIANA S	OLD IN THE	UNITED STATES
ARTICLES	1914	1917
Cacao, crude India rubber, unmanufactured:	\$473,883	\$492,163
Balata India rubber	375,747	398,670 23,639
Sugar, cane	7,617	692,382

#### FRENCH GUIANA

Most of the trading with French Guiana is, under normal conditions, controlled by France, but, as is the

IMPORTS OF CHEMICALS AND ALLIED PI	PODUCTS INTO	FRENCH GUIANA
Articles		
CHEMICAL PRODUCTS	\$14,164	\$10,387
British Colonies	795 13,321	917 9,371
United States PREPARED MEDICINES	15 19,891	11,468
SOAPS AND PERFUMERY EXPLOSIVES	43,188	29,847
Dynamite	2,029	704
Gunpowder On.s, Vegetable	16	2,027
Colza Cottonseed:	80 41,524	116 45,190
United States	37,293	25,675
Castor Coconut	244	278
Linseed Olive	3,493 17,634	2,333 13,306
Other fixed Volatile	125 409	96 290
OILS, MINERAL.	25,669	24,478
COLORS AND DYES	19,034 7,542	6,196
GLASS AND GLASSWARE.	12,719 11,724	11,550 10,964
PAPER AND PAPER WARES France	30,648 30,341	51,761 51,440

case with the other Guianas, it is unimportant. Gold is the most valuable product, the output approximating some two million dollars a year. Primitive methods prevail in the industry. There are important timber resources, as yet but little exploited. Rosewood is exported to France in considerable quantities normally and there used in the manufacture of rosewood extract. This extract is produced to some extent in the colony also. Balata and phosphate rock are exported.

The official statistics of the country prove that chemical products are not imported in large quantities, the preceding table showing such details as are available for 1913 and 1914.

The following table shows that the war has increased the demand for American cottonseed oil in the colony. Even if complete data were available there would probably be no other features sufficiently interesting to note. These are official American figures for the fiscal years 1914 and 1917:

AMERICAN PRODUCTS SOLD	IN FRENCH	GUIANA
ARTICLES	1914	1917
Cement, hydraulic Chemicals, drugs, dyes, medicines Oils:	\$ 34 139	\$ 2,125 780
Mineral—illuminating Vegetable—cottonseed Quicksilver	12,860 27,982	11,439 68,596 5,052

Materials imported into this country from French Guiana are of very little value, and information as to their exact nature is not readily available.

#### VENEZUELA

In the extent of its foreign trade Venezuela is a close second to Colombia among the countries dealt with in this article. The country is sometimes considered as comprising three zones: The Coastal Zone, the principal products of which are coffee, cacao and sugar; the Orinoco River Zone, largely pastoral; and the Forest Zone, from whence come India rubber, balata, tonka beans, vanilla, and copaiba, and in which are found the mineral deposits, which only in recent years have begun to attract foreign capital. Manufacturing is not at all well developed.

Before the war the United States furnished about a third of all the goods imported into the country, but in 1917 the American share was seventeen out of twenty-five millions. In compiling the following table from the original Venezuelan statistics it was not found practicable to show the principal sources of origin for the individual items, but some idea of the extent to which the different competing countries divide the trade can be gained from the entries under "Total of all Imports," which includes all lines imported into Venezuela. As an importer of the finer chemical products Venezuela is rather important. Fiscal years are shown.

VENEZUELAN IMPORTS OF CHEMI	CALS AND ALLIER	PRODUCTS
ARTICLES	1914	1917
TOTAL OF ALL IMPORTS	\$17,005,303	\$25,073,902
France	1,110,961	1,042,170
Germany	2,407,662	
Netherlands	1,696,774	153,000
United Kingdom United States	3,923,836 6,158,122	4,604,419 16,977,644
CHEMICALS, DRUGS, MEDICINES:	0,130,122	10,977,044
Acid, sulfuric	1,058	5,567
Acids, other	34,133	19,481
Calcium carbide	45,881	32,087

VENEZUELAN IMPORTS OF CHEMICALS AND ALLIED PRODUCTS (Concluded) ARTICLES . 1914 1917

ARTICLES .	1914	1917
CHEMICALS, DRUGS, ETC. (Concluded)		
Carbonic acid gas	12,103	13,961
Chemicals, drugs, medicines,	12,105	13,901
D. e. s	550,855	875,032
Disinfectants	30,320	45 929
		45 929
Epsom and Glauber salts	2,295	7,373
Perfumery	131,445	202,153
Quinine	a 2	52,540
Soda, bicarbonates of	3,569	6,390
Soda, common, caustic, crystals.	30,305	68,275
Soda, silicate of	6,246	8,617
COLORS AND VARNISHES: Paints and colors	Service and the service	0
Paints and colors	84,534	119,129
Varnishes	5,855	10,661
Explosives:		
Dynamite	14,523	2,145
Gunpowder	9,689	27,153
OILS, MINERAL:	C THE ADDRESS OF A DESCRIPTION OF A DESC	
Benzene and gasoline	51,632	319,795
Kerosene	190,025	199,252
Lubricating oil	35,279	48,054
Paraffin	1,730	101,798
OILS. VEGETABLE:	Contraction of the second	A GARAGE DE STREET COMPANY
Linseed	17,804	29,387
Olive	119,381	168,581
Other	5,329	6,924
GLASS AND GLASSWARE:	server a state of the server	The second of the second
Bottles	70,306	72,630
Glassware	89,198	54,600
Sheet glass	12,316	18,438
PAPER AND CARDBOARD:	12,010	10,100
Cardboard	32,014	36,405
Paper, printing	36,580	154,298
Paper, all other	177,705	358,697
	111,105	000,097
(a) Not shown separately in 1914.		

The following table for the fiscal years 1914 and 1917 shows that Venezuela is no exception to the rule that South American countries have turned to the United States for chemical and allied products since the war started. Imports of almost all lines have increased in value, some of them in a very marked man-

AMERICAN PRODUCTS SOL	NO STATE FOR DESIGN	A
ARTICLES	1914	1917
Aluminum and manufactures Blacking, including shoe paste Candles Celluloid and manufactures Cement, hydraulic Chemicals, drugs, dyes, etc.:	\$ 51 2,808 8,674 478 48,870	\$ 5,206 5,167 8,393 15,711 69,316
Acids: Sulfuric All other Copper sulfate Dyes and dyestuffs Medicines, patent and proprietary. Petroleum jelly, etc Roots, herbs, barks Soda salts and preparations	473 952 28,877 1,692 173,613 191 254 (a)	5,364 35,382 24,792 8,851 30,101 299,408 3,982 4,067 85,675
All other Explosives: Cartridges, loaded Dynamite Gunpowder All other Flavoring extracts and fruit juices Glass and glassware. Grease:	70,145 70,073 1,267 11,862 5,250 5,101 16,079	434,467 40,572 520 25,740 18,032 8,458 141,738
Lubricating Soap stock and other India-rubber manufactures Ink Leather, patent Metal polish Naval stores Oilcloth and linoleum	4,766 1,934 42,377 6,058 8,551 149 55,508 6,494	13,8147,700224,48714,15684,32612,22159,9777,951
Oils: Mineral: Illuminating Lubricating, etc Gasoline Other light Vegetable: Cottonseed	198,295 26,348 38,652 1,759 1,133	195,932 62,522 287,877 1,114
Linseed Other fixed Volatile Paints, pigments, etc.: Dry colors	3,625 1,106 2,596 2,851	4,342 32,399 6,057 8,739 18,535
Ready-mixed paints Varnish Zinc oxide All other (including crayons) Paper and manufactures Parafin and parafin wax Perfumeries, cosmetics, etc Photographic sensitized goods Plumbago and manufactures	15,348 4,427  23,166 69,804 29 11,998 6,991 411	33,575 7,069 5,066 47,521 483,754 113,551 33,466 13,239 3,762
Soap: Toilet. Other. Stearin, vegetable. Wax and manufactures. (a) Not stated separately in 1914.	18,268 172 332	35,441 824 51,420 7,425

ner, and the problem here is the same as in the other countries—to retain the advantage when European competition returns.

Sugar, india rubber, balata, copper, and "All other chemicals" (including probably tonka beans, vanilla, and copaiba), are the principal items of Venezuelan export to the United States that can be considered of interest to the chemical industry. The extent to which they enter the American market is shown in the following table covering the fiscal years 1914 and 1917:

VENEZUELAN PRODUCTS SOLD IN	THE UNITED	STATES
ARTICLES	1914	1917
Asphaltum and bitumen	425,060	258,205
Bones, hoofs, horns Chemicals, drugs, dyes, etc.:		11,271
Chicle Other gums	28,975	23,324 7,515
All other chemicals	71,056	304,369
Copper	208,364	507,369
Dyewoods, in crude state	1,260	4,086
Fertilizers	11,222	116,709
Fish sounds	7,822	37,404
Hide cuttings and other glue stock India rubber, etc.:	••••	3,518
Balata	211,794	341,220
Guayule gum		3,985
India rubber	128,063	249,867
India-rubber scrap	80	703
Sugar, cane	10	1,126,788

#### PARAGUAY

Imports of all kinds into Paraguay in 1914 totaled only five million dollars, the United States ranking a rather poor fourth after Germany, England, and Argentina as a source of supply. Such export trade as there is consists of animal and forest products, fruits, petitgrain oil, tobacco (a German source of supply), and yerba maté (Paraguayan tea). As the following Paraguayan figures show, the United States has had the advantage in sales of chemicals, drugs, medicines, and explosives, while Germany has been favored in the glass business. The statistics are inadequate and do not represent actual market values.

PARAGUAYAN IMPORTS OF CHEMICA	ALS AND ALLIED	PRODUCTS
ARTICLES	1914	1915
CHEMICALS, DRUGS, MEDICINES Germany United Kingdom United States ARMS, AMMUNITION, EXPLOSIVES Germany United Chetter	1226,528 42,299 33,017 80,961 58,674 12,993	\$113,636 4,159 24,339 50,402 3,532 7
United States GLASS, GLASSWARE, EARTHENWARE France Germany United States	23,342 71,442 10,949 51,410 393	1,156 13,294 3,151 1,326 515

Such details as are available in the American statistics of exports to Paraguay for the fiscal years 1914 and 1917 are shown in the following table:

AMERICAN PRODUCTS SOI	LD IN PARAGUAY	
ARTICLES	1914 .	1917
Blacking, shoe paste, etc Chemicals, drugs, dyes, etc Explosives—loaded cartridges Illuminating oil	\$15,550 17,193 8,394	\$ 2,702 15,050 7,181

As the exports from Paraguay pass through Argentina and Uruguay, and are credited to those countries in our ownofficial statistics, it is difficult to determine the extent to which Paraguayan products are sold in this country, but it is known that quebracho extract and petitgrain oil are received in fair quantities. The tanning-extract industry has developed rapidly in recent years. An item of 1,108 tons of muriate of potash, valued at \$43,161, was recorded as coming from Paraguay in 1914, but it has not appeared since.

# ORIGINAL PAPERS

#### A STUDY OF THE CONDITIONS ESSENTIAL FOR THE COMMERCIAL MANUFACTURE OF CARVACROL

#### By ARTHUR W. HIXSON AND RALPH H. MCKEE

### Received June 21, 1918

Carvacrol is closely related both chemically and physiologically to thymol. The latter substance is used as a specific for hookworm disease and as the principal ingredient in many antiseptic preparations. Hookworm is probably the greatest handicap to the full use and occupation of the tropics by the white races. On account of the general use of thymol in antiseptic manufacture and the widespread organized effort being made in many countries to combat the enormous inroads of the hookworm disease, the demand for it has become so great that the supply from present sources is entirely inadequate.

Attempts have been made to produce thymol synthetically, but up to the present time no process of any promise commercially has been developed.

Recent comparative tests1 have shown carvacrol to be practically equal to and, in some cases, to possess greater antiseptic value than thymol. Its importance as a substitute for this substance is sufficient to warrant an investigation of its production.

Carvacrol is found as an ingredient in the essential oils of many labiate plants and particularly in those of the species Origanum. There are two kinds of Origanum oil<sup>2</sup> known commercially, namely, Trieste oil containing from 60 to 85 per cent of carvacrol, and Smyrna oil containing from 25 to 60 per cent. Both of these oils contain cymene. Carvacrol is also found in the oil of thyme from Thymus vulgaris in which it sometimes replaces all of the thymol.<sup>3</sup> The quantity of carvacrol available from these natural sources, however, is very small and of practically no commercial importance. These facts indicate that if carvacrol is to be used in the place of thymol a process for its synthetic preparation on a commercial scale must be developed. The prospects were such as to encourage a study of the synthetic preparation of carvacrol and the conditions essential for its commercial production, which is the object of this research.

Carvacrol was first prepared synthetically by Schweizer<sup>4</sup> who found that the same oil was obtained by treating caraway oil with potassium hydroxide, phosphoric acid, or iodine. Claus<sup>5</sup> heated camphor with iodine and obtained a product which he called camphor-creosote which was identical with the product made by Schweizer. Müller<sup>6</sup> while comparing cymene and thymol obtained from different sources, sul-

<sup>\$</sup> Ber., 2 (1869), 130.

fonated pure cymene, made the sodium salt, fused it with sodium hydroxide and obtained an oil which he identified as carvacrol. Kekulé and Fleischer<sup>1</sup> treated carvone obtained from caraway oil with orthophosphoric acid and produced carvacrol. From cymene, obtained from camphor, Pott<sup>2</sup> made potassium cymene sulfonate, which he fused with potassium hydroxide. He poured the fusion mass into water, neutralized with sulfuric acid, and obtained a small amount of yellowish liquid which distilled at 230° C. He recognized it as an isomer of thymol. He also observed that if a few drops of an alcoholic solution of the oil were added to a solution of ferric chloride, a characteristic green coloration would be produced. Reychler<sup>3</sup> found that when carvo-chlorhydrate is distilled, hydrochloric acid split off and the distillate contained carvacrol. Etard<sup>4</sup> treated monochlorcamphor with a 10 per cent solution of zinc chloride and heated it. By distilling the mass and agitating the distillate with caustic soda he obtained carvacrol. Mead<sup>5</sup> and Kremmers converted pinene into nitroso-pinene and by hydrolyzing this substance produced carvacrol. The yield was about 60 per cent. Wallach6 made amidothymol from oxydihydrocarvoxime, treated it with sulfuric acid, and found carvacrol to be one of the products. Harries' passed steam for a long time over hydrobromcarvone and produced a small amount of carvacrol. McKee<sup>8</sup> has patented a process for the manufacture of carvacrol based upon the use of spruce turpentine as the source of cymene.

A careful examination of these methods showed that in each case, with the exception of that of McKee, the raw materials used were of such a nature as to make them impracticable for the production of carvacrol on a commercial scale. However, the discovery that spruce turpentine consists mainly of cymene and the fact that it is produced in large quantities as a by-product in the manufacture of wood pulp by the sulfite process indicated that a method, along the line suggested by the experiments of Müller, Pott, and McKee might be capable of commercial development. For these reasons an investigation was made to determine whether a method based upon the following reactions could be carried out on a commercial scale:

I-Formation of cymene I-sulfonic acid by treating spruce turpentine with sulfuric acid.

II-Removal of the excess sulfuric acid used in (I) and formation of calcium cymene sulfonate by treatment with finely divided limestone.

III-Formation of sodium cymene sulfonate in solution and removal of calcium as carbonate by treating with soda ash.

- 1 Ber., 6 (1873), 1087.
- 2 Ibid., 9 (1876), 468.
- 3 Chem. Centr., 63 (1892), 379.

6 Ann., 291 (1896), 348.

<sup>8</sup> U. S. Patent No. 1,265,800, May 14, 1918.

<sup>&</sup>lt;sup>1</sup> The average results of four viability tests using the organisms B. typhosus, B. communior, and staphylococus pyogenes aureus, furnished through courtesy of Dr. A. K. Balls, Department of Bacteriology, College of Physicians and Surgeons, Columbia University, and Dr. A. M. Buswell, Department of Chemical Engineering, Columbia University, New York City.

<sup>&</sup>lt;sup>2</sup> U. S. Dispensary, 19th Edition, 1905, 1432.

<sup>\*</sup> Ibid., 19th Edition, 1905, 1571.

<sup>&</sup>lt;sup>4</sup> J. prakt. Chem, **24** (1841), 257. <sup>5</sup> Ibid., **25** (1842), 264.

<sup>&</sup>lt;sup>4</sup> Compt. rend., **116** (1893), 1136. <sup>5</sup> Am. Chem. J., **17** (1895), 607.

<sup>7</sup> Ber., 34 (1901), 1924.

IV—Formation of sodium carvacrolate by fusing the sodium cymene sulfonate with caustic soda.

V—Formation of carvacrol by treating the fusion products of (IV) with sulfuric acid.

A study of these basic reactions indicated that the following fundamental operations would be necessary: I—Sulfonation of cymene.

2-Disposal of the sulfonation products.

3-Formation of calcium cymene sulfonate solution and precipitation of calcium sulfate.

4-Filtration and disposal of the filter cake.

5—Formation of sodium cymene sulfonate solution and precipitation of calcium carbonate.

6-Filtration and disposal of filter cake.

7-Evaporation of the sodium cymene sulfonate solution and disposal of the solid salt.

8—Fusion of the solid sodium salt with caustic alkali.

9—Disposal of the fusion products.

10—Neutralization of the fusion product solution and formation of carvacrol.

11-Separation of the carvacrol.

12-Purification of the carvacrol.

#### EXPERIMENTAL

The experimental work consisted of the determination of the relative importance of the preceding operations and the conditions under which they could be carried out with maximum efficiency.

MATERIALS—All of the materials used in the experimental work were of standard commercial purity, such as can always be obtained on the market without difficulty in normal times, with the exception of spruce turpentine, which up to this time, although produced in large quantities as a by-product, has had no commercial value.

The spruce turpentine used was a steam-distilled product obtained from the New Process Gasolene Company, of Philadelphia, and was purchased in the crude form by that company from the J. and J. Rogers Company, of Au Sable Forks, N. Y. This product was clear and nearly white. After remaining in the laboratory for several months a distinct yellow tinge appeared. The product was used in the "as received" condition without treatment of any kind. A fractional distillation of 1.5 liters gave the following results:

Temperature Degrees C.	Fraction Cc.	Per cent
Below 171.5	. 50	3.33
171.5-178.5		83.34
Above 178.5	. 200	13.37

Kertesz<sup>1</sup> found spruce turpentine to contain 80 per cent of cymene, from 10 to 12 per cent of sesquiterpene, and the remainder diterpene. The fractionation results show that nearly 80 per cent of the material came off at about 175° C., the boiling point of cymene.

SULFONATION—The prime variables in this operation are (a) strength of acid, (b) temperature, (c) time, (d) proportional amount of acid, (e) amount of stirring, (f) type of sulfonating vessel.

STRENGTH OF ACID—The adoption of 66° Bé. sulfuric acid as the most practical strength for the sulfonation of benzene in phenol manufacture led to the

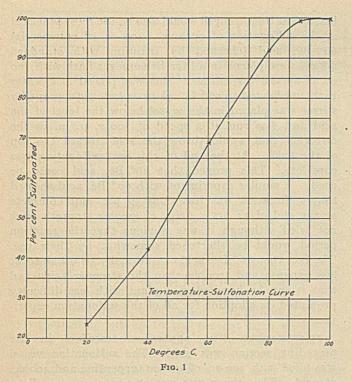
belief that this strength would also be the most practical in the sulfonation of cymene. 400 cc. of commercial 66° Bé. acid (checked by titration with standard alkali) were placed in a liter Erlenmeyer flask with 200 cc. of spruce turpentine. This was placed in a water bath and heated to 96° C. A two-blade glass propeller stirrer was placed in the vessel below the level of the acid and was run at a speed of 700 r. p. m. in the direction that would throw the acid toward the top of the flask. At the end of  $3^{1/2}$  hrs. sulfonation was complete. This proved that 66° Bé. acid could be used. A similar experiment with 60° Bé. acid showed that sulfonation was less than 50 per cent complete at the end of 12 hrs. Acids of greater strength were not tried although it was obvious that the reaction period would be shortened somewhat by their use. The fact that 66° Bé. acid can normally be obtained at less expense and trouble than the stronger acids and that it can be handled in a plant with less difficulty prompted its adoption for all of the sulfonation experiments.

TEMPERATURE—The apparatus described in the preceding section was used. The sulfonation vessel was filled with 200 cc. of spruce turpentine and 400 cc. of acid. The stirrer was run at 700 r. p. m. Four hours was the standard time. At the end of the reaction period the stirrer was removed and acid allowed to settle and separate from the cymene and the sulfonated portion. The upper layer was then siphoned off, shaken well, and 25 cc. removed by means of a pipette. This was placed in a graduate and 75 cc. of water added, shaken well, and allowed to stand for 12 hrs. The unsulfonated cymene formed a layer at the top and its volume was read directly. The following table and curve, Fig. 1, show the results:

	TABLE I	
Temp. ° C.	Unsulfonated portion Cc.	Per cent sulfonated
20	19.3	22.80
40	14.5	42.00
60	7.8	68.80
80	2.0	92.00
90	0.2	99.20
100	Trace	99.5+

The rate of sulfonation varied almost directly with the increase of temperature up to 90°. Between this temperature and 100° C. the rate was highest, indicating that the temperature should be kept within this range for efficient sulfonation. This temperature being near the boiling point of water makes it an easy one to maintain in both laboratory and plant. Sulfur dioxide is evolved at all temperatures. The amount was slight at low temperature and increased as the temperature was raised.

TIME—With the same apparatus and the same quantities of materials, time experiments were run. The data in the preceding table indicate that a temperature between  $90^{\circ}$  and  $100^{\circ}$  would give the shortest time required for complete sulfonation.  $96^{\circ}$  C. was chosen for the reason that it was convenient to maintain. The extent to which the reaction had proceeded was determined by the same means used in the preceding experiments, that is, 25 cc. portions were taken from the upper layer which had been separated



from the acid and, after diluting and standing for 12 hrs., the volumes of the unsulfonated portions were read. The results are given in Table II.

	TABLE II	
Time Hrs.	Unsulfonated portion Cc.	Per cent sulfonated
$\frac{1/2}{2}$ 3 4 5	18.4 12.4 4.3 1.2 0.1	26.40 50.40 82.80 95.20 99.60
5	Trace	99.6+

These data show that a 4-hr. period is sufficient for complete sulfonation at  $96^{\circ}$  C. with efficient stirring. The results are shown graphically in Fig. 2.

AMOUNT OF ACID REQUIRED—200 cc. charges of spruce turpentine were sulfonated at 96° C. with quantities of acid varying from 400 cc. to 150 cc. Sulfonation was complete with amounts down to 200 cc. With amounts below this complete sulfonation could be obtained, but the time required was greatly increased. Many batches were run using equal volumes of acid and cymene and complete sulfonation was obtained in 4 hrs., with the temperature at 96° C. These results show, contrary to previous records, that a volume of 68° Bé. acid equal to that of the cymene is sufficient. It is to be noted also that the decrease in the amount of acid used to the equal volume limit did not decrease the rate of reaction.

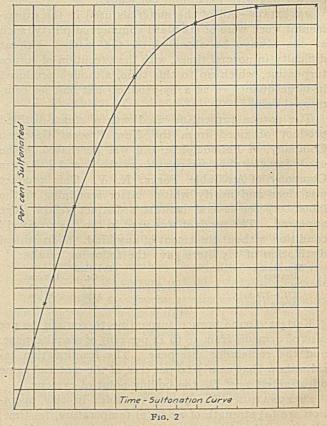
AMOUNT OF STIRRING—McKee<sup>1</sup> has shown that the rate of sulfonation of hydrocarbons is distinctly dependent upon efficient stirring, other things being equal. By increasing the efficiency of his stirring device he was even able to sulfonate kerosene with ease. No experiments were made to determine the effect of different degrees of stirring upon the rate of sulfonation of cymene, but the type of stirrer used, the speed at which it was run, and the shape of the

1 Science, 35 (1912), 388.

reaction chamber insured an extremely intimate contact of reacting materials.

TYPE OF SULFONATING VESSEL-To determine whether a cast iron or steel sulfonating vessel could be used, one was made by screwing a cast iron cap on the lower end of a 6 in. length of 4 in. pipe. A similar cap provided with stuffing-box openings for a stirrer and the thermometer was used for a cover. A two-blade stirrer of the propeller type was used. The blades were set at such an angle that when run at speeds above 500 r. p. m. the liquid was thrown against the cover of the vessel. To the stem a series of pulleys of different diameters was fastened in order to use different speeds. The stirrer was driven with an electric motor. A thermometer was placed in the vessel at such a depth as to be well in the liquid, and it was held in place by a stuffing-box similar to that used for the stirrer. When the cover was screwed on well the vessel was gastight. The vessel was set into a water bath to such a depth that the surface of the water came to the lower edge of the cover. The water bath was heated by an ordinary Bunsen burner and the temperature was controlled within two degrees without difficulty.

With this apparatus many runs using 300 cc. of spruce turpentine and 300 cc. of acid were made. The temperature in all cases was from 96° to 98°. With the stirrer running 500 to 600 r. p. m. sulfonation was complete in from  $3^{1}/_{2}$  to 4 hrs. A larger amount



of sulfur dioxide was given off than with the glass vessel. When all openings in the cover were tightly closed, a considerable pressure was developed. It was observed that although a considerable surface of the sulfonator was above the surface of the water, the temperature inside of the vessel during the opera-

tion was less than one degree below that of the bath. When the sulfonation products were poured into a glass vessel and allowed to cool, a white solid settled to the bottom of the acid layer. This was found to be ferric' sulfate. "The iron had reacted with an excess of concentrated sulfuric acid forming ferric sulfate and sulfur dioxide. This accounted for the increased amount of sulfur dioxide observed during the reaction period. The amount of ferric sulfate formed varied from 3.55 to 5.6 g., representing a loss of iron of from 0.73 to 1.57 g. The weight of the sulfonator was 3500 g. The loss was quite small and undoubtedly in a larger vessel of special cast iron would be still less on account of the relatively smaller contact area and refractory skin on the surface of the vessel. The presence of this iron was not objectionable. If for any reason its removal might be desired this could be done at practically no increase of cost by the addition of a small quantity of lime just after the precipitation of the calcium sulfate in the next operation.

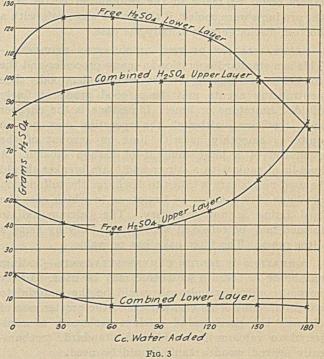
SULFONATION PRODUCTS-When sulfonation was complete and the mixture allowed to stand for a short time, two distinct layers formed. The lower, lighter colored layer contained the greater portion of the excess sulfuric acid and about 20 per cent of the total amount of the cymene sulfonic acid. The upper, darker colored layer contained the greater part of the cymene sulfonic acid, some sulfuric acid, and materials resulting from the action of the acid on the impurities in the spruce turpentine. The formation of the layers took place rapidly when the materials were hot. When cold, the upper layer became very thick and viscous. When allowed to stand for a few days at 20° C. the cymene sulfonic acid began to crystallize and finally the whole layer became solid. With the temperature below 10° C. the upper layer solidified very rapidly. Colorless, transparent crystals of cymene sulfonic acid, isolated from the upper part of the lower layer, melted at 50° to 51° C. This was the melting point found by Spica<sup>1</sup> and later by Eaton and McKee<sup>2</sup> for a cymene sulfonic acid of the composition C10H13SO3H.2H2O, which the latter two made from spruce turpentine. All of the constituents of the upper layer were found to be soluble in water with the exception of a small amount of a very finely divided white substance which settled out after standing for a number of days. Examination of this white precipitate showed it to be sulfur. Evidently it came from the complete reduction of a small portion of the sulfuric acid.

DISPOSAL OF SULFONATION PRODUCTS—The formation of two distinct layers which could easily be separated suggested that a recovery of the unused sulfuric acid might be possible. The problem was to recover the sulfuric acid without losing the cymene sulfonic acid which was present in considerable quantity in the lower layer. Inasmuch as it was necessary to add water in the next operation, experiments were made to determine whether the distribution of the substances in the layers was affected by dilution.

1 Ber., 14 (1881), 653.

<sup>2</sup> Unpublished thesis, University of Maine, 1911.

For these experiments 150 cc. of spruce turpentine and 150 cc. of 66° Bé. acid were used in the sulfonation. When sulfonation was complete the hot products were poured into a 500 cc. graduate and allowed to stand until the volumes of the layers became constant. After reading the volumes a definite quantity of water was added and the mass shaken until the mixing was complete. The mixture was then allowed to stand until the volumes became constant again. 10 cc. samples were taken with a pipette and analyzed. The total acid content was determined by titrating with standard sodium hydroxide. The free sulfuric acid was determined by precipitation with BaCl<sub>2</sub>.



The difference between these gave the sulfonic acid content which was calculated as sulfuric acid. The results are given in Table III and are shown graphically in Fig. 3.

Set of the la		TABLE III			
Water added Cc.	Free H2SO4 lower layer G.	Free H <sub>2</sub> SO <sub>4</sub> upper layer G.	Combined H2SO4 lower layer G.	Combined H <sub>2</sub> SO <sub>4</sub> upper layer G.	
None 30	108.16 124.88	· 49.22 40.73	19.94 11.89	85.19 94.24	
60	123.60	36.57	6.54	97.30	
90 120	121.03 116.43	39.87 45.38	7.59 7.62	98.15 96.96	
150 180	99.39 79.06	58.68 82.70	7.63 6.50	97.93 98.64	

These results show that by the addition of a quantity of water equivalent to one-fifth of the total volume (approximately 300 cc.) the combined sulfuric acid, which represents the cymene sulfonic acid, dropped from 19.94 g. to 6.54 g. in the lower layer and increased from 85.19 g. to 98.15 g. in the upper layer. After this the values remained practically constant with further dilution. The values given in the above table for the combined sulfuric acid represent approximately the percentages of cymene sulfonic acid in the two layers.

The dilution experiments were carried out to the point where the two layers merged; analyses at these dilutions were not made for the reason that the acid was not worth recovering. Although it was possible to reduce the cymene sulfonic acid content in the lower layer 60 per cent, the amount which still remained was such that its loss probably more than balanced the value of the acid recovered and the amount of ground limestone saved. Market and plant conditions will be the deciding factors. If the acid is recovered the conditions that will give the lowest cymene sulfonic acid loss should be used. At that dilution the acid would have a concentration of about 60° Bé. and could be used to neutralize the fusion mixture in a later operation. The separation of the layers could be made in the sulfonation kettle after the products were cooled, if the kettle was made with a bottom discharge as is usually the case.

NEUTRALIZATION OF THE SULFONATION PRODUCTS— This is a standard operation in many processes and the conditions controlling it are well understood. The neutralizing agents may be a good grade of finely divided limestone or lime. Limestone is the cheaper and is efficient, although the operation does not go quite as smoothly as with lime on account of the evolution of a large amount of carbon dioxide. A lead-lined tank with a stirrer and foam breaker should be used unless care is taken to discharge the sulfonation products into a slurry of limestone in which case the lead lining is not necessary. The calcium sulfate formed may be removed without difficulty by using a filter press. The filter cake has no value.

FORMATION OF SODIUM CYMENE SULFONATE—Sodium carbonate or sodium hydroxide may be used. Under normal conditions soda ash would be the material to use on account of its cheapness and the greater ease of filtering the precipitated calcium carbonate as compared to calcium hydroxide. A standard, mechanically stirred wooden tank should be used.

SIMULTANEOUS NEUTRALIZATION OF SULFONATION PRODUCTS AND FORMATION OF SODIUM CYMENE SUL-FONATE SOLUTION-This may be done by neutralizing partially or completely the sulfonation products with limestone and then adding the requisite amount of soda ash. By this method the calcium sulfate and calcium carbonate can be removed by a single filtration. This procedure requires closer chemical control than when the two operations are separated for the reason that it is much more difficult to tell when the reaction with the soda ash is complete. Unless close watch is kept on this operation under plant conditions an excess of soda ash will often be used by the workmen. It is doubtful if this combined procedure will work out as well as the former in plant practice as the resulting saving in limestone and labor will be small.

EVAPORATION OF THE SODIUM CYMENE SULFONATE SOLUTION—It is obvious that the use of as little water as possible in the preceding steps will save time and expense in the production of dry sodium cymene sulfonate. This salt is very soluble in water and its water solutions are difficult to evaporate to dryness at atmospheric pressure. The presence of a small amount of water causes the salt to form a thick pasty mass which becomes liquid above 70° C. This last portion of solvent may be removed, in plant practice, by either drying in vacuum or by use of a film dryer such as the drum dryers (atmospheric pressure or vacuum) which have lately come into such wide use in drying concentrated or pasty substances in chemical plants.

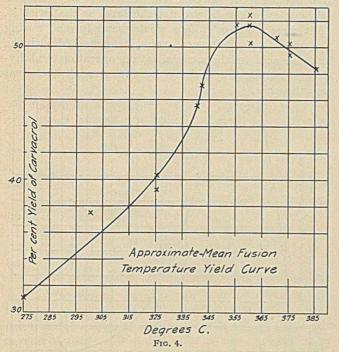
FUSION OF THE SODIUM CYMENE SULFONATE—The problem was to determine (a) the best fusion reagent, (b) the proper fusion temperature, (c) the most suitable type of fusion kettle, (d) the time required for completion of the reactions, and (e) the minimum amount of fusion reagent for maximum yield.

The apparatus used for the preliminary fusion experiments consisted of a cylindrical steel vessel  $4^{1/4}$ in. in diameter and 5 in. deep. The steel was 3/16 of an inch thick. The cover was a steel plate with openings for a stirrer shaft and thermometer and could be closed tightly by means of stove bolts and winged nuts. It was necessary to have the stirrer work through the whole mass of the liquid in order to break up surface crusts and prevent the material from sticking to the bottom and sides of the kettle. The vessel was heated with a Fletcher burner. After making a number of fusions with this apparatus it was obvious that it was not possible to control the temperatures closely enough. To overcome this difficulty the fusion vessel, equipped as described, was placed in an insulated bath containing about 20 lbs. of a eutectic mixture of sodium and potassium nitrates. This bath, provided with a propeller type stirrer, was heated with a Fletcher burner. With this arrangement there was no difficulty in keeping the temperature constant within one degree. The difference between the temperature of the bath and that inside of the fusion chamber was less than one-half degree when the stirrers were running.

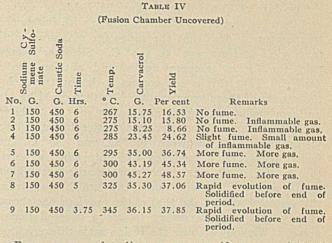
FUSION REAGENT—Heretofore, those who have prepared carvacrol by a fusion method have used potassium hydroxide in large excess. Although scientific literature favors the use of this reagent for the fusion of sodium cymene sulfonate and similar salts, such as sodium benzene sulfonate, modern commercial practice on the latter has demonstrated that caustic soda can be used with equal efficiency and at much less expense. For this reason a good grade of commercial caustic soda was used in all of the fusion experiments.

FUSION TEMPERATURE—To determine what effect temperature has upon the efficiency of the fusion operation, fusions were made at different temperatures. The charges consisted of 150 g. of dry sodium cymene sulfonate and 450 g. of caustic soda. The fusion period was 6 hrs. The caustic soda which melted at  $319^{\circ}$  C. was fused first. To this the sodium cymene sulfonate (in granular form) was slowly added. At the end of the fusion period the products were poured gradually into 2 liters of cold water, forming a strongly alkaline solution which was neutralized by adding dilute sulfuric acid ( $40^{\circ}$  Bé.). The carvacrol set free in this operation was extracted with benzene. After separation of the benzene solution from the neutral liquors, the benzene was distilled off and recovered. The residue was distilled yielding carvacrol and a tarry residue. The carvacrol was weighed, and the yield thus obtained was used as the criterion by which the efficiency of the fusion operation was determined.

As the sodium cymene sulfonate dissolved in the molten caustic the temperature at which the mass remained molten rapidly fell. The average time required to get a smooth fusion was one-half hour. It was possible to lower the fusion temperature to  $255^{\circ}$  C. and still have the mass molten enough to stir well. If a quantity of water equal to 10 per cent of the weight of the caustic was added, the fusion took place much more smoothly and the mixture was kept molten at a still lower temperature. However, the addition of water was of no advantage for the reason that its rapid evolution as steam at higher temperatures made it difficult to keep the molten material in the fusion chamber until it was all given off. When  $280^{\circ}$  C.



was reached (fusion vessel uncovered) a bluish white fume was observed. This increased in amount rapidly with the rise of temperature until at 325° C. it was quite dense. The mass thickened under these conditions and at the end of the fifth hour it was granular and would not pour. If the temperature was kept below 300° C., although some fume was evolved, the material remained liquid until the end of the fusion period and poured well. At 280° C. when a flame was held in the upper part of the fusion chamber a flash was observed. As the temperature was raised the flash became more pronounced and at 300° C. the gas burned for a number of seconds. At 325° C. it burned longer. With the fusion chamber open at temperatures from 275° to 300° C. the yield of carvacrol varied from 8.25 to 43.19 g. Above 300° C. the yields varied from 35.30 to 45.27 g. and, though higher than for temperatures below 300° C., were very erratic and difficult to duplicate. These facts are revealed by the data in Table IV.



From 150 g. of sodium cymene sulfonate a yield of 95.25 g. of carvacrol should have been produced. The percentage yields in this table and those following were calculated on this basis.

Above 300° C. there was less variation in the yields. This and the fact that the yields were higher led to the belief that still higher temperatures might give better results. It was also noted that when the fusion chamber was covered no fume was evolved; but as soon as the cover was removed it appeared, showing that there was a reaction with the oxygen of the air. To determine whether this reaction was in any way responsible for the great variation in yields, a series of fusions was made at different temperatures with the fusion chamber closed. The cover with an opening and connections for a condenser was screwed down tightly after each charge was inserted. A Liebig condenser provided with an air-tight receiver was attached. From one opening in the receiver a tube ran to a gas holder. With the exception of the cover and the accessories mentioned, the conditions for this series were the same as for the previous one. The data and results are given in Table V and shown graphically in Fig. 4.

#### TABLE V

#### (Fusion Chamber Covered)

Charges consisted of 150 g, sodium cymene sulfonate and 450 g, caustic soda. Fusion period, 6 hrs.

No.			Vield Per cent	Remarks
1	275	29.65	31.13	6.5 cc. H <sub>2</sub> O and trace of yellow oil distilled off. Small amount of inflammable gas.
2	300	35.71	37.41	6 cc. H <sub>2</sub> O, 15 cc. amber colored oil. Oil fluorescent.
3	325	37.16	39.01	6.5 cc. H <sub>2</sub> O, 21 cc. amber colored oil. Oil fluorescent. About 3 liters gas.
4	325	38.20	40.10	8 cc. water, 22 cc. amber colored oil. Fluores- cent. Passed gas through bromine. No re- action.
5	340	43.57	45.74	9 cc. water, 25 cc. amber colored oil. About 4 liters gas. Oil less fluorescent.
6	342	44.81	47.04	7.5 cc. water, 23.5 cc. oil. Oil amber colored and fluorescent.
7 8	355 360	49.36 48.33		Lost distillate. 9 cc. water, 22 cc. amber colored oil. Fluores- cent.
9	360	49.91	52.31	9.5 cc. water, 23 cc. oil darker colored and more fluorescent.
10	360	49.14	51.60	11 cc. water, 22 cc. amber colored oil. Fluores- cent. When cover was removed, mass flashed.
11	370	48.26	50.65	11 cc. water, 22 cc. lighter colored oil. Not quite as fluorescent.
12	375	47.92	50.31	14 cc. water, 22 cc. amber oil. Oil fluorescent. When cover was removed, mass ignited.
13	375	46.97	49.31	11 cc. water, 22.5 cc. amber colored oil. Fluorescent. When cover was removed, mass ignited.
14	385	46.10	48.39	10.5 cc. water, 22 cc. amber colored oil. Oil fluorescent. Mass did not ignite when cover was removed.

The data of Table V show that the yields of carvacrol increase and become more uniform with the rise of temperature. Also that the range for maximum uniform yield is from 350° to 370° C. Schorger<sup>1</sup> states that the fusion temperatures should not be above 300° C. That this is not correct is demonstrated by the results of these experiments. Neither could he get uniform yields at temperatures below 300° C. Above 370° C. decomposition becomes noticeable and the yields decreased. Between 360° C. and 370° C. the fusion mass had a tendency to ignite when exposed to the air. This was much more marked at higher temperatures. A comparison of the data obtained from this series of fusions and that of the previous one shows plainly that it is necessary to use -a covered fusion vessel. Without a cover the fusion mass thickens, due to reaction with oxygen of the air, and the volatile oil which distils off is lost.

It was noted that in all of the fusions an amber colored, fluorescent oil came off. The quantity distilled from the different fusions was quite constant. It varied somewhat in color and in the degree of fluorescence with different fusions. As a rule it became darker on standing. In some instances it became more fluorescent, and in others less, when exposed to the air for some time. A quantity of this oil was carefully fractionated; 75 per cent of it boiled between  $172^{\circ}$  C. and  $178^{\circ}$  C. This fraction was water-white and had the odor and characteristics of cymene. The higher boiling fraction varied in color from light straw to very dark brown and was relatively small in amount. All of the fluorescent material boiled above  $210^{\circ}$  C.

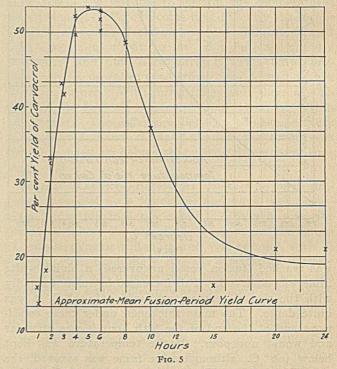
To verify the belief that the oil was principally cymene, the fraction boiling between 172° C. and 178° C. was sulfonated in the usual manner. The sodium salt was made and fused with caustic soda. Fifty grams of the sodium yielded 10 g. of carvacrol and 3.5 cc. of an amber colored, fluorescent oil similar to that described. This proved that the oil which distilled from the cymene sulfonate was essentially cymene. Inspection of the results of this series of fusions shows that the cymene recovered in the distillate from the fusions represents a decomposition of from 18 to 20 per cent of the sodium cymene sulfonate fused. Experiments showed that this cymene could be easily recovered and re-used. On a factory scale its recovery would be profitable. The presence of sodium sulfate in considerable quantity as one of the fusion products along with cymene seemed to indicate that two reactions took place between the sodium benzene sulfonate and the caustic soda, one of which formed sodium carvacrolate and sodium sulfite, the other cymene and sodium sulfate. However, the evolution of hydrogen and methane and the formation of a considerable quantity of tarry matter indicated that other reactions took place.

The gas evolved during the fusions varied in quantity from 2 to 4.5 liters. Samples from two fusions were analyzed and were found to contain hydrogen and methane. There were no traces of carbon monoxide, oxygen, or unsaturated hydrocarbons.

<sup>1</sup> THIS JOURNAL, 10 (1918), 259.

	TABLE VI	
Gas from Fusion No.	Hydrogen	Methane
(Table V)	Per cent	Per cent
3	78.16	21.84
6	80.00	$20.00$ } by volume

To get some idea of the stability of sodium cymene sulfonate 150 g. (containing 0.57 per cent moisture) were placed in the fusion kettle alone and heated. Between 345° and 350° C. it melted and showed no signs of decomposition. The temperature was gradually raised to 375° C. and at this temperature a distillate consisting of  $13^{1/2}$  cc. water and 7 cc. of a dark oil came over during the first hour. The heating was continued for 3 hrs. During the entire period hydrogen sulfide came off in large quantities. The mass gradually thickened and was sticky and black when poured. The oil from this salt was somewhat similar to that obtained from the fusions with caustic soda except that it was smaller in amount, very much darker in color, and was saturated with hydrogen sulfide. The hydrogen sulfide formed showed that the reaction without caustic soda was not the same as that with it. If it were, sodium sulfide would have formed during the fusion. This, in turn, would have reacted with the sulfuric acid in the neutralization operation and hydrogen sulfide would have been evolved. Such was not the case.



TIME REQUIRED FOR FUSION was determined by making a number of fusions with the temperature and the composition of the charges constant using the quantities of carvacrol as the criteria. The results appear in Table VII and Fig. 5.

Fusion periods of from 4 to 6 hrs. gave the best results. With longer periods the yields gradually fell off and were more or less erratic. The same was true for the shorter periods. The curve in Fig. 5 shows the relation between the length of fusion period and the yield of carvacrol. The products of the 15, 20, and 24 hr. periods were dry, granular masses when removed from the fusion chamber. On exposure to air they gradually became hard and stony. In the cases of the 20 and 24 hr. fusions the products were liquid up to within 2 hrs. of the end of the periods. The amount of distillate was practically the same for all of the fusions of more than 2 hrs. duration, showing that the consistency of the products at the end of the period was in no way related to it.

TADEN VIT

soda.	nperature,	000 C. 1	50 g. sodium e	cymene sulfonate, 450 g. caus
No.	Time Hrs.	Car- vacrol G.	Percentage Vield of Carvacrol	Remarks
1 2 3 4 5 6 7 8 9 10 11 12 13 14	1 1.5 2 2 3 3 4 4 5 6 6 6 8	$\begin{array}{c} 15.15\\ 13.71\\ 17.21\\ 31.15\\ 31.43\\ 39.78\\ 41.14\\ 47.12\\ 49.36\\ 49.81\\ 49.91\\ 49.33\\ 49.14\\ 46.31 \end{array}$	$\begin{array}{c} 15.90\\ 13.39\\ 18.07\\ 32.59\\ 32.99\\ 41.76\\ 43.19\\ 49.47\\ 51.82\\ 52.29\\ 52.31\\ 50.14\\ 51.60\\ 48.69 \end{array}$	Liquid when poured, Liquid when poured,
15 16 17 18	10 15 20 24	35.41 15.41 20.01 20.10	37.17 16.18 21.01 21.10	Remelted after 5 hours. <sup>1</sup> Remelted after 5 hours. <sup>1</sup> Remelted after 5 hours. <sup>1</sup>

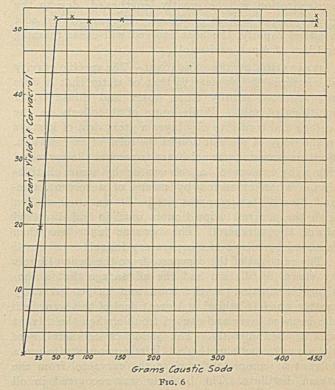
QUANTITY OF FUSION REAGENT REQUIRED—In all of the fusions made in the previous experiments a large excess of caustic soda was used. To ascertain the minimum amount required for the highest carvacrol yields and the best working conditions, fusions were made with different quantities. The results are given in Table VIII and Fig. 6.

TABLE VIII

		ure, 36	0° C. 150 g	s. sodium cymene sulfonate. Fusion period,
6 hrs.				
			Percentage	
	Caustic	Car-	Yield	
	Soda	vacrol	Carvacrol	
No.		G.	G.	Remarks
1	450	49.91	52.31	Distillate 9.5 cc. water, 23 cc. oil.
1 2 3	150	48.12	50.52	Distillate 9 cc. water, 22 cc. oil.
3	100	48.95	51.39	Distillate 9 cc. water, 23 cc. oil.
4	75	48.50	50.92	Distillate 11.5 cc. water, 22 cc. oil.
4568	50	49.50	51.96	Distillate 11 cc. water, 22 cc. oil.
6	25	18.97	19.91	Distillate 7 cc. water, 17.5 cc. oil.
8	0	00.00	00.00	Distillate 13.5 cc. water, 7.5 cc. black oil.

It is interesting to note that the quantity of the fusion reagents could be reduced almost to the theoretical amount required without much effect. upon the carvacrol yields. With less than 100 g. the mass could not be poured from the kettle. With smaller amounts the products were of a pasty consistency and had to be scraped out. It is quite necessary that the contents of the kettle be discharged rapidly in order to prevent excessive loss due to reactions which take place on exposure to the air. These reactions were so rapid that ignition took place on two occasions. This was especially true when the fusion products were semisolid. The results of the fusion in which no caustic soda was used have been discussed previously.

FUSION OF CALCIUM CYMENE SULFONATE—It is possible to fuse calcium cymene sulfonate with caustic alkali and obtain carvacrol. Schorger<sup>1</sup> obtained his highest yield by using this salt. Although one filtration and the soda ash required for the making of the sodium salt, would be saved, more caustic would be necessary for the fusion; and mechanical difficulties, resulting from the insoluble calcium sulfite formed during fusion, would be experienced, thus over-balancing the advantage of the process.



Two fusions using calcium cymene sulfonate were made with the following results. The charge consisted of 80 g. of caustic soda and 80 g. of calcium cymene sulfonate. The temperature was 360° C.

No.	Carvacrol G.	Per cent of Theoretical Yield	Remarks
1	14.82	28.80	16.5 cc, of fluorescent oil and 11 cc. of water distilled during fusion. Fusion was thick when poured.
2	17.70	34.41	14 cc. of fluorescent oil and 13 cc. of water came off during fusion. Fusion quite thick when poured.

The oil which distilled from the fusion was identical with that obtained from the fusions of the sodium salt. Although the two fusions were made under the same conditions, there was quite a perceptible difference in the yield of carvacrol.

NEUTRALIZATION OF THE FUSION PRODUCTS-The fusions were poured into 2 liters of water and allowed to dissolve. To this solution dilute sulfuric acid (40° Bé.) was added in sufficient quantity to neutralize the excess caustic soda and free the carvacrol from the sodium carvacrolate. When the acid was added in excess it reacted with the sodium sulfite formed during the fusion, and sulfur dioxide was evolved. This served as a means of determining when the neutralization was complete. It was necessary to add the acid to the solution by leading it through a tube to the bottom of the vessel. If this was not done an excess of acid on the surface reacted with the sodium sulfite in that part of the solution before neutralization throughout was complete. The appearance of sulfur dioxide under such a condition was not evidence that neutralization was complete. If the excess sulfuric acid were recovered at the end of the sulfonation

operation it could be diluted and used for this purpose. If concentrated acid is used, the time required for neutralization will be greatly lengthened, due to the great amount of heat produced. If concentrated acid is added rapidly, the heat evolved will cause foaming and loss of much carvacrol.

SEPARATION OF THE CARVACROL—The specific gravity of carvacrol lies so near to that of water that it does not separate readily from water and dilute water solutions of salts. While some of it collects on the surface and forms an oily layer a great deal of it stays in the body of the solution in the form of an emulsion. For this reason it was necessary to remove the carvacrol either by means of a solvent or by steam distillation. When extracted by means of a solvent, onehalf liter of benzene was used. It was well shaken with the neutral fusion liquors until it had dissolved all of the carvacrol. The benzene layer was then removed by means of a separatory funnel.

The removal of the carvacrol from the fusion liquors by steam distillation had the advantage that a considerable portion of the solid and suspended tarry matter was left behind. A great deal of this went into the benzene layer and caused trouble when the solvent was applied directly. The yields of carvacrol were the same by both methods. It was necessary to use a solvent to completely remove the carvacrol from the steam distillate. The benzene was recovered in all cases and it was found that an average of 4 per cent was lost in the extraction and distillation. When an excess of acid was used in neutralization a large amount of sulfur dioxide formed was taken up by the benzene.

After the removal of the benzene the residue containing the carvacrol was distilled. The carvacrol came over in the form of a clear, light yellow oil between 227° C. and 245° C., leaving a tarry residue which averaged 0.25 g. for each gram of carvacrol. It was noted that when the yields of carvacrol were low the quantity of tar extracted was also low. The amount of the residue depended upon the method used for removing the carvacrol from the fusion liquors. When the steam distillation method was used the quantity of tar was much smaller. If the carvacrol is extracted directly by means of a solvent, a still with a bottom discharge should be used for the distillation of the extract. This would provide for the removal of the tarry residue when it was hot. If allowed to cool it formed a hard, brittle mass.

PURIFICATION OF THE CARVACROL—This was done by redistilling the product obtained from the fusion liquor by either of the two methods mentioned. No difficulty was experienced in getting a product with a fairly constant boiling point.

#### LARGE SCALE EXPERIMENTS

Having determined the optimum conditions for the several operations involved in the production of carvacrol from spruce turpentine on a laboratory scale, it was desirable to test them by using larger quantities of materials. Accordingly this was done with apparatus of semi-commercial size.

SULFONATION-Fifty-three pounds of spruce turpen-

tine were treated with 114 lbs. of 66° Bé. sulfuric acid for 6 hrs. at 98° C. in a cast iron sulfonation kettle. The time was longer than would have been necessary had the kettle been equipped with a thoroughly efficient stirring apparatus.

REMOVAL OF THE EXCESS SULFURIC ACID—No attempt was made to recover the excess acid. The sulfonation products were slowly poured into a 150 gal. wooden tank containing a slurry of limestone (95 per cent passed 100 mesh). On the basis of the spruce turpentine containing 80 per cent cymene the calculated amount of limestone required was 95.2 lbs. The quantity needed for complete neutralization was 102 lbs. The neutral solution was filtered with a 12 in., 12-plate Sperry press.

PRODUCTION OF SODIUM CYMENE SULFONATE—To the filtrate from the liming operation 16.5 lbs. of 58 per cent soda ash (58 per cent Na<sub>2</sub>O) were added. The calculated amount was 17.1 lbs. The calcium carbonate formed was removed by filtration and the clear solution was evaporated in a 50 gal., steam jacketed, open iron kettle to a thick, sticky consistency. The salt was dried in a steam-jacketed shelf vacuum dryer to a moisture content of 0.7 per cent.

The yield was 70.5 lbs. of dry sodium cymene sulfonate. The calculated yield was 74.8 lbs. In factory practice the sodium cymene sulfonate solution should be evaporated to saturation with a vacuum and then finished with a film drum dryer.

FUSION OF THE SODIUM SALT—Forty pounds of 76 per cent caustic soda (76 per cent Na<sub>2</sub>O) were fused in a 30 in. cast iron fusion kettle heated with gas. To the fused caustic 70.5 lbs. (calculated to dry basis) of sodium cymene sulfonate were slowly added. The kettle was tightly covered, the condenser connected, and the temperature gradually raised to  $350^{\circ}$  C. The temperature was kept between  $350^{\circ}$  and  $360^{\circ}$  C. during the 6 hr. fusion period. At  $270^{\circ}$  C. the fluorescent oil began to distill. The rate at which it came over increased as the temperature was raised. The fusion went smoothly and poured readily. Less caustic could have been used without the substance solidifying during fusion. The salt was poured into an iron tank containing 30 gal. of water.

NEUTRALIZATION OF THE FUSION LIQUOR—Dilute sulfuric acid (40° Bé.) was slowly added until the fusion liquor was neutral. 67.5 lbs. of acid were required. The calculated amount was 70.32 lbs. The operation was carried out in a steel tank.

SEPARATION OF THE CARVACROL—Forty-five pounds of benzene were thoroughly agitated with the neutral fusion liquors. The benzene solution was separated by drawing off the water solution from below. The benzene (43.75 lbs.) was recovered by distillation with a steam-jacketed still. The benzene loss was 2.7 per cent.

There being no direct heated still of sufficient size available, I liter of the extract was distilled in a distilling flask. The product obtained was slightly fluorescent and contained a little finely divided carbon which came from the cracking of the tarry substance. When redistilled a clear, yellowish oil that boiled at 232° C. was obtained. From the quantity of carvacrol obtained the total yield was calculated. The data and results of the large scale experiments are given in Table IX.

TABLE IX-DATA AND RESULT	TS OF	LARGE	SCALL	Expr	RIMEN	rs
		Theo- retical				
	Quan-	Quan- tity		0-	Quan- tity	Per cent
	tity	Re-	1.2	Yield	Recov	- Re-
MATERIALS	Used	quired	Yield	Per	ered	cov-
AND PRODUCTS	Lbs.	Lbs.	Lbs.	cent	Lbs.	ered
Spruce Turpentine	53		Sec. 24			
Sulfuric Acid (66° Bé.)	114	32.2				
Limestone	102	95.2	17.000	1000		Sec.
Soda Ash		17.1				
Sodium Cymene Sulfonate				94.25		1000
Caustic Soda		23.9			and the second	
Sulfuric Acid (40° Bé.)		70.32				Case OS
Benzene	45				43.75	97.3
Fluorescent Oil (recovered for re-use)			7.3			
Sp. Gr. = 0.8890 Carvacrol			25.3	57.2		
Tar	1000		3.8		1.000	1.1.1
	WT No. Inc. Street	TELL STATES	And the second second	COLUMN STREET	all a second as	Without Start 1

DISCUSSION OF RESULTS AND OBSERVATIONS

The most favorable conditions for the various operations as determined in the laboratory when applied on a larger scale gave similar results. With the greater quantities of materials the conditions were more easily controlled. This was especially true of the fusion operation which was the most difficult one in the process to handle. The quantity of the cymenebearing oil obtained from the fusion, per unit of sodium cymene sulfonate fused, was smaller than that obtained from laboratory experiments. From the latter it amounted to about 20 per cent of the original cymene used and from the former to 13.7 per cent. The apparatus required to collect this oil is simple and inexpensive and the quantity of the oil given off is such as to make its recovery imperative.

When the caustic soda was fused first and the sodium salt added afterwards, trouble was experienced with foaming unless the salt was added very slowly. However, this procedure may be used if the cover of the kettle is such that it can be opened and closed quickly so as to prevent oxidation and loss of the distillate. When the sodium salt and the caustic were well mixed together previous to charging, no trouble with boiling over during the fusion was experienced. The stability of the sodium cymene sulfonate permitted this to be done. The fusion kettle, however, should be of ample size to take care of the temporary swelling of the fusion mass.

When dry sodium cymene sulfonate was exposed to the air it took up moisture rapidly and became sticky. This property would prevent it from being stored in an open bin.

The time required for each operation was such that it could be completed within 8 hrs., the ordinary working day. This would be an important factor in plant operation.

The yield of carvacrol from the operations with the larger quantities of materials was about 5 per cent greater than with the quantities used in the small scale experiments. If the cymene recovered from the fusion operation is taken into consideration, as should be done, the carvacrol yield will be increased. The difference this makes is shown in the following table. The cymene content of the original spruce turpentine and of the oil recovered was taken as 80 per cent in each case. The cymene content of the recovered oil was subtracted from that originally taken. From this the theoretical yield and the percentage yields were calculated.

No. (Table V)	ered Oil into	Per cent Yield Taking Recov- ered Oil into Consideration	Increase	
• 7	51.71	63.94	12.23	
8	50.14	62.60	12.46	
9	52.31	64.65	12.34	
10	51.60	63.65	12.05	
11		62.51	11.86	
Large scale experiment	57.2	66.4	9.2	

Carvacrol can be produced by the process outlined with the same equipment as that used in a plant for the manufacture of phenol or beta-naphthol, with but few changes. A fusion kettle equipped with a close fitting, easily opened cover and a water-cooled coil condenser would be necessary. In addition to this a direct heated still for the distillation of the carvacrol would be essential. Otherwise the phenol or betanaphthol plant could be used as it is.

Inasmuch as practically the same plant can be used, the cost of production of carvacrol can be compared with that of phenol. The United States Government has fixed the price of phenol at 38 cents per lb. This is commonly known to give the manufacturer an average net profit of 7 cents per lb., thus making the total average cost 31 cents per lb. The total material cost per pound of carvacrol produced on the basis of 60 per cent yield would be about 35 cents per lb. The labor and overhead costs would be higher than those of phenol due to the lower yield obtained. The overhead cost would also be somewhat higher on account of the extra equipment required. The total cost per pound of carvacrol produced would be close to 60 cents, a cost well within the limits of commercial possibility.

#### SUMMARY

A process for the manufacture of carvacrol from cymene has been outlined and studied in detail.

The process depends upon the use of spruce turpentine as the source of cymene.

The optimum conditions for the necessary operations have been determined.

Briefly stated, the process consists of:

I—Making cymene sulfonic acid by thoroughly agitating spruce turpentine with an equal volume of  $66^{\circ}$  Bé. sulfuric acid at a temperature of  $90^{\circ}$  to  $100^{\circ}$  C. for 4 hrs. in a cast iron sulfonating kettle.

2-Neutralization of the excess sulfuric acid, formation of calcium cymene sulfonate in solution by adding ground limestone to the sulfonation products and removal of the calcium sulfate formed by filtration.

3—Formation of sodium cymene sulfonate by adding soda ash to the hot calcium cymene sulfonate solution and removal of the precipitated calcium carbonate by filtration.

4—Concentration of the sodium cymene sulfonate solution in a vacuum evaporator to the point of saturation.

5-Precipitation and drying of the calcium cymene sulfonate by means of a rotary steam heated film dryer, or other suitable means. 6—Fusion of the dry sodium cymene sulfonate with approximately one-half of its weight of 76 per cent caustic soda in a cast iron or steel fusion kettle provided with a cover and water-cooled condenser at a temperature of 350° to 370° C. for 6 hrs.

7—Pouring the fusion products into a minimum amount of cold water and neutralization of the solution so formed by adding just enough 40° Bé. sulfuric acid to neutralize the excess caustic soda and set free the carvacrol from the sodium carvacrolate.

8—Separation of the carvacrol from the neutral fusion liquid by steam distillation or by agitating with a solvent such as benzene.

9-Recovering the solvent by distillation.

10-Distillation of the carvacrol from the benzene extract with a direct heated still.

II-Purification of the carvacrol by redistillation with the same still.

This process was tested on a large scale which gave even better results than those obtained with the smaller quantities.

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### THE SEEDING METHOD OF GRAINING SUGAR

By H. E. ZITKOWSKI<sup>1</sup> R eceived June 17, 1918

There is a disposition in some quarters to deny to the sugar industry its claim as a member of the chemical industrial family. That the beet sugar industry, the direct descendant of scientific research and probably the oldest member of magnitude of the chemical industry family, should find it necessary to establish any claim in this direction is anomalous. Someone, sometime, as a labor of love, will bring this out as a matter of record.

Here I desire merely to state that nowhere else in industry has technical accounting been carried to the point that it has in the beet sugar industry. The beet sugar industry has taken laboratory manipulations or processes such as dialysis or diffusion, precipitation, filtration, evaporation, and crystallization and adopted them to factory scale, handling millions of pounds of material daily, and with a refinement which taxes the ingenuity of the most expert manipulator to now duplicate on a laboratory scale.

It is even held that the beet sugar industry, which established itself in Europe during the Napoleonic wars, deserves to a very large degree the credit for the rapid development of the chemical industry of Germany. It was the beet sugar industry which furnished the technically trained and experienced men, capable of transferring laboratory reactions and processes to a factory scale and keep the commercial requirements in mind, when the modern chemical industry sprang into being.

Men go so far as to state that it was the beet sugar industry of Germany which made possible the terrible war that Germany is waging, not only because it was the foundation stone for the chemical industry but also because the cultivation of the beet brought with <sup>1</sup> Paper read before the American Institute of Chemical Engineers, Berlin, N. H., June 19, 1918. it scientific agriculture which doubled the agricultural yields, thereby making Germany largely self-sustaining and eliminating the threat of being starved to submission by blockade. There is much that can be said in defense of such a view-point.

However, at this time here it is desired to discuss briefly the large scale practical application of the well known "seeding" method of inducing crystallization.

The oldest, and for many years the only method of producing sugar crystals was to concentrate the properly purified sugar-bearing syrups to the required density or supersaturation and set them away. In the course of days, or weeks, or even months, as the solution cooled', sugar would crystallize out. Even after the introduction of the vacuum pan method of "boiling" sugar, for many years this was the only method and was known as "boiling blanks." Sometime during the fifties of the last century the art or rather the "trick of the trade" of "graining" sugar while yet in the vacuum pan was acquired, though this was not generally adopted till 20 years later, and even up to this day frequently, for reasons which need not be discussed here, blanks are boiled. The general procedure at present is as follows:

A quantity of the properly prepared sugar-bearing syrup with a water content of from 30 to 40 per cent is introduced into a vacuum evaporator or "pan" and is concentrated till saturated. At this point the boiling mass will be at a temperature from  $70^{\circ}$  to  $80^{\circ}$  C., and under a vacuum of from 20 to 25 in.

Under certain conditions aqueous sugar solutions have the property of forming supersaturated solutions and in the presence of the non-sugars or impurities, such as occur even in purified juices, this tendency is greatly increased, so that in factory practice it is always necessary to carry the concentration to some degree of supersaturation before crystallization occurs. Now it is not to be inferred that in all cases simple supersaturation will bring about crystallization, for, if the content of non-sugars or impurities in the solution is great enough, crystallization will not occur even though evaporation be carried to the point of dryness.

Under the normal conditions of sugar manufacture, however, that degree of supersaturation is finally reached at which crystal formation begins. Sometimes a sudden shock applied to the boiling, supersaturated mass is resorted to in order to induce crystallization, such as a sudden raising of the vacuum bringing with it violent ebullition, or the introduction of a hot syrup of a lower density which has the same effect, or the injection of steam or air into the mass. No matter how produced, at the moment of their formation the crystals are infinitely small and some time is required to attain a visible size, though this may be only a few . moments. Eventually the crystals formed do become visible and then the critical moment of the "boiling" of the "pan" arrives.

It becomes the attendant's business to allow the formation of crystals to proceed till, in his judgment, the proper number of nuclei for the apparatus in question have formed, then to arrest the formation of further crystals by lowering the supersaturation coefficient, which is done by lowering the vacuum, raising the temperature and diluting with syrup of a lower density. From then on it becomes his business so to regulate the temperature, the rate of evaporation, and the introduction of syrup that the minute crystals will grow, and, when the pan is full, be of the size to supply the market's demand.

Not much time for deliberation is available when it is realized that often a pan holding 200,000 lbs. of mass and yielding 80,000 lbs. of granulated sugar is boiled complete in less than 2 hours. If the operator's judgment at the time of "graining" is at fault, and he allows the formation of too many crystals, the final product will be too small, may cause great difficulties in separation from the mother liquor and decrease the yield; if the number of crystals formed is too small the resulting end-product will be too large, the time for crystallization will be longer, and again the yield will be reduced. In both instances the cost of production is increased.

But even at best the crystal formation at the time of graining is not instantaneous, and by the time that some have reached a visible size others are at the point of formation, therefore infinitely small, with the result that the final end-product is not uniform in size. This is objectionable, not only on economical ground, as the difficulty of separating the sugar crystals from the adhering mother liquor is greatly increased by uneven grains, but also a fastidious consuming public demands not only a pure, white, sparkling crystal of a certain size (varying somewhat in different parts of the country) but the crystals must also be fairly uniform in size.

The above points out briefly some of the problems in connection with producing the "granulated" crystals usually found on our markets. Not all of the sugar produced is, however, so directly obtained as granulated. Much of the final output is first obtained as a "raw" or impure sugar, which is melted, reprocessed and recrystallized. The liquors from which these raws are obtained are of a lower purity and therefore present greater difficulty to crystal formation or "graining." The impurities present, however, must not be above a certain ratio to the sugar present or crystallization in the pan will be entirely prevented and the mass will be blank, or if crystals form they will remain so small as to be separated from the surrounding mother liquor only with great difficulty, if at all.

Eventually a final liquor, molasses, remains, which in beet sugar manufacture may contain 50 per cent of sucrose but also sufficient of impurities to prevent further crystallization. Any procedure, therefore, which increases the quantity of sugar recoverable by direct crystallization, or which increases the yield with each crystallization, or reduces the time element, or even merely simplifies the procedure, may be very valuable. The saving may amount to only one hundredth of a cent per pound of sugar, and yet, on the quantity of sugar produced, run into astonishing totals. A very valuable recent development in the art of boiling sugar is the "seeding" of the saturated mass in the vacuum pan with sugar dust to serve as nuclei for the sugar crystals, instead of the method above described of bringing about spontaneous crystal formation or "graining" by high supersaturation. Considering the simplicity of the use of sugar dust for this purpose and that it can be used without an expense or alteration of any kind in the equipment, this method is likely to prove to be one of the most valuable developments introduced into the industry in recent years.

While the method of "seeding" herein considered is a recent development, yet the principle underlying it is not at all new.

In U. S. Patent No. 489,879 dated January 10, 1893, covering a Process of Obtaining Sugar, is found the following:

"It has, however, long been known that if such impure solutions are brought in contact with a sufficiently large number of crystals, a very effective crystallization can be brought about in the vacuum pan; and this knowledge has been made practical use of in sugar factories by the addition of raw sugar crystals to juices which could otherwise only be boiled with great difficulty. Similarly it is sometimes customary in sugar refineries, when very small crystals are desired, to bring the liquor to the crystallization point, and then by the introduction of a quantity of finely pulverized sugar to start energetic crystallization, thus insuring the formation of small crystals by shortening the time of boiling and consequently that given to the crystals in which to grow."

Similar references to "seeding" sugar can be found at even earlier dates, and yet it appears very doubtful that this method was ever successfully used in producing marketable sugar until less than two years ago.

To Mr. John C. Bourne, now somewhere with the Canadian forces, belongs the credit of having called attention to this subject, which led to the present development. Mr. Bourne was not familiar with the literature on the subject and was not aware that the idea had ever been suggested—to him it was entirely new.

The method as at present used very successfully, is as follows:

The sugar-bearing syrup properly prepared is introduced into the vacuum pans and under the usual conditions of vacuum and temperature is concentrated till the point of saturation has been passed, that is, till the solution is slightly supersaturated or, in the language of the industry, till it reaches a light "string proof." At this point a quantity of sugar dust or powdered sugar, varying from 1/2 qt. to 2 qts. for each rooo cu. ft. of vacuum pan capacity, is introduced by aspiration, through suitable connection, beneath the surface of the boiling mass, care being taken to prevent the inrush of any considerable quantity of air, as otherwise a portion of the sugar dust introduced is likely to rush up with the air and on into the condenser. This operation requires not more than half a minute. One or two minutes are required for the sugar particles introduced to mix through the boiling mass. For several minutes after the introduction or "seeding" the usual "proof" appears blank or at best simply shows a cloud, the sugar particles introduced being too small to be visible to the naked eye.

The solution, however, is supersaturated and is boiling vigorously and the crystals or fragments of crystals introduced immediately begin to grow and soon show up on the "proof." Evaporation is continued till about that density is reached usually obtained by the older methods of "graining." From here on the procedure is as usual except that experience has shown that less difficulty will be experienced to keep out false grain or "smear" in a "seeded" pan than one "grained" by the older method.

The essential difference between the two methods is that in the one case the crystallizing nuclei are introduced ready made, in the other are formed spontaneously by highly supersaturating the liquor which carries with it certain objectionable features as previously pointed out.

The quantity of sugar dust to be used per unit volume of pan capacity is dependent on the size of the dust particles and on the size of crystals required in the finished product.

In the writer's experience the "seed" used was such sugar dust as accumulates in the usual dust collectors of the sugar drying equipment. In size the dust particles ranged from an impalpably fine powder to particles just passing through a standard Tyler sieve of 100 mesh. Particles larger than this were screened out. In some instances powdered sugar as found on the market was used with success.

As a great difference in size or volume exists between particles or crystals just passing through a roomesh sieve and particles impalpably fine, it was considered that perhaps superior results would be obtained if the dust or "seed" used was more uniform in size. With this thought in mind trials were made with dust from which both the coarser and finer materials had been removed; improved results were obtained only if the seed did not contain too many particles larger than 80 mesh.

While at the time of seeding a vast difference in size and weight exists between a powder particle and a particle of 100 mesh, when these nuclei have reached the market size little difference exists. In all probability the rate at which the crystallizing sugar deposits on the nuclei is in direct proportion to their surface areas. The surface area of an impalpably fine particle in proportion to its volume is so immensely greater than that of a particle of 100 mesh that as the two particles grow, the smaller growing at a relatively faster rate than the larger, the difference in size will become negligible.

Then, also, possibly the tendency of crystal splinters to regenerate the original shape of the crystals from which they have been produced may play a rôle, as the finer particles especially are largely crystal splinters. This describes briefly the new method of "graining" sugars in the vacuum pans as practiced for the first time during the past campaign in a dozen or more beet sugar factories of the Western States. It deserves further study before all the factors are determined. However, the results obtained during the past campaign in the factories coming under the writer's observation, especially on the lower products, were uniformly superior to the normal results.

ROCKY FORD, COLORADO

#### A STUDY OF SOURCES OF ERROR INCIDENT TO THE LINDO-GLADDING METHOD FOR DETERMINING POTASH

By T. E. KEITT AND H. E. SHIVER Received June 19, 1918

Prior to our study<sup>1</sup> of the DeRoode method for the determination of potash in fertilizer materials, much data had been accumulated in this laboratory relative to sources of error incident to the Lindo-Gladding method for determining potash. In the interest of furthering the adoption of the modified DeRoode method we deem it advisable to present the results of these studies. In fact, the work on the DeRoode method was undertaken, primarily, because of the inaccuracies of the Lindo-Gladding method.

The determination of water-soluble potash in all samples reported in Table I was done by the official Lindo-Gladding method.<sup>2</sup> Another set of determinations was made exactly as outlined under the modified official method.<sup>3</sup> Still another set of determinations was made on these samples by the modified official method,<sup>4</sup> except that hydrochloric acid was not added to the filtrate nor was the ammonia and ammonium oxalate added after the solution had been made to volume and an aliquot of 100 cc. (equivalent to one gram) had been taken.

This was done in order that the ammonia precipitate and the lime might be separately estimated. The aliquots were brought to boiling and ammonia was added until alkaline, the boiling continued a few minutes to expel any considerable excess of ammonia, then the precipitate was separated by filtering hot and washing with hot water. The combined filtrate and washings from each determination was then evaporated to a volume of about 200 cc., made alkaline with ammonia, and precipitated with ammonium oxalate; the calcium oxalate precipitate was filtered after standing over night, and thoroughly washed with hot water. The combined filtrate and washings from each of these precipitations was then used for the determination of potash. In evaporating these filtrates, as well as all other large filtrates that have much salts of ammonia present, there is a decided tendency to crawl. This can be controlled by acidifying with I : I sulfuric acid, and filling the dishes only to within a quarter of an inch of the top. The volatilization of the ammonium salts was also accom-

<sup>1</sup> THIS JOURNAL, 10 (1918), 219.

<sup>2</sup> A. O. A. C., U. S. Dept. of Agr., Bureau of Chem., Bull. 107 (revised).

<sup>3</sup> U. S. Dept. of Agr., Bureau of Chemistry, Bull. 152. <sup>4</sup> Ibid.

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panied with difficulties on account of the large amount of residue and the danger of spurting. After we began adding the sulfuric acid before evaporation was complete, this trouble was greatly lessened.

Т	TABLE I- INFLUENCE OF IRON AND ALUMINUM IN SOLUTION ON THE ESTIMATION OF POTAS H												
SAMPLE No.	Per cent Potash (K2O), Li nd o- Gladding Method	Per cent Potash (K <sub>2</sub> O), Modified Lindo - Gladding Method	Per cent Potash (K <sub>4</sub> O), Revised Modified Lindo- Gladding Method	Per cent of Ammo- nia Precipitate	Per cent Calcium Oxide (Calc.)	Difference between Lindo - Gladding and M od i fi e d Method	Difference between Lindo - Gladding and Revised Mod- ified Method	Difference between Modified Lindo- Gladding and Re- vised Modified Method					
1214 1216 1218 1220	3.89 2.63 1.69 4.16	$\begin{array}{r} 4.04 \\ 2.60 \\ 1.62 \\ 4.30 \end{array}$	4.00 2.60 1.71 4.55	$0.77 \\ 1.05 \\ 1.55 \\ 2.43$	$\begin{array}{c} 0.13 \\ 0.34 \\ 0.95 \\ 0.15 \end{array}$	-0.15 0.03 0.07 -0.14	$-0.11 \\ 0.03 \\ 0.07 \\ -0.39$	$0.04 \\ 0.00 \\ -0.09 \\ -0.25$					

Table I shows that in comparing three methods for determining water-soluble potash, the essential feature of difference in the methods being the bulk and method of handling of the ammonia precipitate and the lime, the only large difference in results is correlated with the amount of ammonia precipitate, which consists mainly of hydrates of iron and of aluminum. These hydrates constitute a bulky, sticky, gelatinous precipitate, the influence of which will be proved later.

From the data already outlined, we were led to believe that some of the potash is occluded by the bulky precipitate formed on the addition of ammonia and ammonium oxalate. To test this point we procured ten samples that had been found deficient in potash by the Fertilizer Control.

The method of procedure was as follows: 10 grams of each sample were boiled with 300 cc. of distilled water for 30 min., then filtered into a 500 cc. volumetric flask to separate from the insoluble material. The residue was washed with hot water, and the combined filtrate and washings, about 350 cc., were brought to boiling, and ammonia and ammonium oxalate added as directed for the Lindo-Gladding method.<sup>1</sup> The solutions were cooled, made to a volume of 500 cc., and filtered rapidly by means of a suction pump to separate the ammonia and ammonium oxalate precipitate, the filtrate being used for the determination of potash.

TABLE II-VOLUME OF FILTRATE, AMOUNT OF POTASH RECOVERED IN FILTRATE, AMOUNT OF POTASH WASHED OUT OF RESIDUE, TOTAL POTASH DETERMINED, AND THE EFFECT OF DILUTION BEFORE PRE-CIPITATION ON POTASH CONTENT

		Offi	CIAL M	ETHOD			METHODS
No.	s of Filtrate 500 cc.	cent Potash O) Calc. on cc. Volume	r cent Potash (K <sub>2</sub> O) in the Washings	cent Potash O) in Washings c. on Difference ween Volume 500 cc.	r cent Total Water - Soluble Potash (K2O) Determined	cent Water- uble Potash O) Diluted ore Precipi- ion	r cent Water- Soluble Potash (K20) not Di- luted before Pre- cipitation
SAMPLE	Volume of J from 500	Per co (K2O 500 c	Per ci (K20 Wasl	Per cent (K2O)inV Calc.onD Between and 500 c	Per cer Water Potash Detern	Per cent Soluble (K <sub>2</sub> O) before tation	Pe
38 160. 547	478 463 483	3.15 2.71 5.98	$     \begin{array}{r}       0.13 \\       0.18 \\       0.24 \\     \end{array} $	2.95 2.69 7.06	3.28 2.89 6.22	3.13 2.72 5.92	3.05 2.64 5.91
850 1229 1387 1389	478 475 470 483	2.68 2.93 1.87 3.13	0.17 0.29	3.86 5.80	2.85 3.22	2.71 2.84 1.85 3.15	2.72 2.76 1.82 3.06
1991 2170 2473	483 470 465 482	3.04 3.05 4.09				2.74 3.12 4.28	2.68 2.95 4.16

Other determinations of water-soluble potash were made by the revised modified Lindo-Gladding method, <sup>1</sup> Loc. cil. which has already been discussed in detail. In making these determinations, two aliquots were taken from each flask, one of which was precipitated with ammonia and ammonium oxalate in the volume of the aliquot, 100 cc., while the other was diluted before precipitation. All were filtered and thoroughly washed, potash being determined in the combined filtrate and washings in each case.

Table III clearly brings out the compensation effects of decreased volume and of occluded potash. It also shows the relation of the volume in which the precipitation with ammonia and ammonium oxalate takes place, to the occlusion of potash.

The ammonia and ammonium oxalate precipitates on the filters which had been thoroughly washed to remove potash, were each placed in a soil digestion flask with 100 cc. hydrochloric acid (sp. gr. 1.115) and digested at the temperature of boiling water until solution was complete. The solutions were transferred to 500 cc. flasks, cooled, and made to volume. An aliquot was taken, diluted to 400 cc., reprecipitated, brought to boiling, and filtered. This operation was repeated twice, making three precipitations in all. The potash from each precipitation was determined separately, in order that we might determine when the separation was nearing completion. The results were so surprising that we had all of the work duplicated. Due to the large amount of work entailed, we used only five samples.

1	ABLE	III-Occ				THE F	RECIPIT	TATE FO	RMED OI	N
				OF AMMO		Аммо:	NIUM O	XALATE		
		Per ce	ent Potas	eprecipi-	Soluble Column	50	able lad-	ol-lo ied	lo-ol-	
		tati	ons of t	the Am-	In	Kat	oluble Glad	rected olume II	S-I U	
		mon	nia and	Ammo-	S, O	B,	0-0-0	e loi	L. L.	
			m Oxala tate, in		er-	ash	er-	abl Coa	Va.n	
			ume.	400 cc.	12 at	Total Potash ed	Litho	Her	N N N	
	No.				PH2		et a	of tas	of ota	
		itt	t.	U	sh	ble	Mshit	H But	din Put	
	SAMPLE	ys Ke	ys ist	Averag	Tace	er cent Soluble Recover	cent otas	cent e Po Dim umn	adine	
	IW	Analys Ke	Anal R	ver	HA'S	RSSH	dip	Col	Gtebr	
			Ŷ	A,	Per 5	P	Pe	A PEO	Pero	
	58	0.91	0.89	0.90	3.28	4.18	3.15	3.99	0.84	
	160 547		0.61 0.62	0.60 0.65	2.89 6.22	3.49 6.87	2.71 5.98	3.23	0.52 0.66	
	850		0.62	0.65	2.85	3.46	2.68	3.31	0.63	
	1229		0.74	0.69	3.22	3.91	3.10	3.71	0.61	

Table III shows that in each case more than 0.5 per cent of potash was occluded by the ammonia and ammonium oxalate precipitate, showing that there are grounds for the manipulators' contention that the Lindo-Gladding method of analysis does not account for all of the potash added in the water-soluble form. It further shows that the Lindo-Gladding method does not account for all of the potash soluble in water at the time of the analysis.

To secure additional information regarding the errors due to the occlusion of potash and diminution in volume incident to the Lindo-Gladding method, pure salt solutions were prepared as follows:

Solution 1 contained potassium chloride and ferric sulfate equivalent to 5.99 per cent K<sub>2</sub>O and 10.31 per cent Fe<sub>2</sub>O<sub>3</sub>.

Solution 2 contained potassium chloride and tricalcium phosphate equivalent to 5.99 per cent K<sub>2</sub>O and 10 per cent Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>.

Solution 3 contained potassium chloride, iron, and tricalcium phosphate equivalent to 5.99 per cent  $K_2O$ , 10.31 per cent  $Fe_2O_3$ , and 10 per cent  $Ca_3(PO_4)_2$ .

TABLE IV-	ERROR	s Du	E TO	DIMINI	SHED VOI	UME ANI	TO Occ	LUDED H	OTASH W	HEN PUP	E SALTS	ARE USI	D		
stock		ate	uot	otash lc. on indo-	(K20) olume	(0]	a0) ita-	(K <sub>2</sub> 0) from cipita-	from cipita-	ash in	tash ered cipi-	Potash overed rmina-	ash tion	20)	by By
	de	Filtr	Aliq	Pot		Vate Vate uot	fro fro ecipit	Ū	<b>A</b> 1	Potash uble in	Potash covered precipi-	Pot	. Potash Solution	(K	(K ddin
each on us	Made	of ]	of	of cc.,	Potash Actual Vo	tash sh W Aliqu	otash vered Repre	epr	tash ered tepr	Wt. Soli	Vt. Re Re	Nt. Ree Deto	Wt. in S	tash cove	tash cove Glac
litti	Ime	olume	olume	(O pp	Po Act	. Potash Wash W me Aliqu	A O H	Pot cove	Pot COV(	21	All V All All ions	All VIII All	otal V (K2O)	Po	Pot Rec
Vol. of eac	Volume	Volı	Volu	Wt. Kge Gla	Wt. on	Wt. Po in Wa Same	Wt. Re. Ist tioi	Wt. 1 Reco 2nd tion	Wt. Rec 3rd tion	Total (Kro Wate	Total V (K2O) by All tations	tion tio	Tot	Wt. not	Wt. not Lin
	Cc.	Cc.	Cc.	Gram	Gram	Gram	Gram	Gram	Gram	Gram	Gram	Gram	Gram	Gram	Gram
25 cc. KCl	500	500	50	0.0304	0.0304					0.0304		0.0304	0.0311	0.07	0.07 .
50 cc. KCl	500 500	500 485	50 50	0.0611 0.0279	0.0611 0.0288	0.0006	0.0002	0.0001	0.0004	0.0611 0.0285	0.0007	0.0611 0.0292	0.0621 0.0311	0.10 0.19	0.10 0.26
25 cc. KCl, 50 cc. FeCla	500	475	50	0.0537	0.0565	0.0020	0.0009	0.0001	0.0007	0.0557	0.0017	0.0574	0.0621	0.47	0.64
25 cc. KCl, 50 cc. Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> 50 cc. KCl, 100 cc. Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	500 500	478 475	50 50	0.0279 0.0549	0.0292 0.0578	0.0009	0.0006	0.0002	0.0004 0.0005	0.0288	0.0012 0.0016	0.0300 0.0587	0.0311 0.0621	$0.11 \\ 0.34$	0.23 0.50
25 cc. KCl, 50 cc. Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> , 25 cc. FeCl <sub>2</sub>	500	475	50	0.0263	0.0277	0.0006	0.0019	0.0003	0.0005	0.0269	0.0027	0.0296	0.0311	0.15	0.42
50 cc. KCl, 100 cc. Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ,							Salar and								Statistics.
50 cc. FeCla	500	468	50	0.0521	0.0557	0.0006	0.0008	0.0002	0.0005	0.1529	0.0015	0.0544	0.0621	0.77	0.92

Solution 4 contained potassium chloride, iron, tricalcium phosphate, and aluminum sulfate equivalent to 5.99 per cent  $K_3O$ , 10.31 per cent  $Fe_2O_3$ , 10 per cent  $Ca_3(PO_4)_2$ , and 10 per cent  $Al_2O_3$ .

These solutions were intentionally exaggerated as to content of impurities and were analyzed in the same manner as already described for the mixed fertilizers. The determinations shown are the first and only results obtained, emphasizing the ease and accuracy of the method of determination.

Table IV shows that the precipitate formed by the addition of ammonia and ammonium oxalate in the flask considerably diminishes the volume when tricalcium phosphate, ferric hydroxide, or a combination of the two are present. It further shows that some of the retained potash may be washed out with hot water, but that a considerable amount cannot be removed in this manner. Three successive reprecipitations in large volumes, dissolving the precipitate each time in hydrochloric acid and reprecipitating with ammonia, show a small amount of potash recovered. In the case of the potash, a larger amount was recovered in the third reprecipitation than in the second, indicating that a continuation of these reprecipitations might have shown a greater recovery. A comparison of the theoretical potash content with the amount determined shows slightly more occlusion by the amount of iron used than by the tricalcium phosphate, although the latter showed marked properties in this respect; a combination of the two increases the occlusion.

#### CONCLUSIONS

This work proves that there are two sources of error in the Lindo-Gladding method for determining potash: (1) the volume of the solution is decreased by the bulk of the precipitate formed on addition of ammonia and ammonium oxalate, which makes a plus error, and (2) the potash in solution is decreased by occlusion of potash by the heavy gelatinous precipitate formed. These two sources of error are partially compensating.

It is impossible to wash out with hot water the potash occluded within the precipitate.

The occluded potash may be separated to a certain extent by repeatedly dissolving the precipitate in hydrochloric acid, diluting to a large volume, precipitating with ammonia and ammonium oxalate, filtering, and determining potash in the filtrates and washings.

The use of pure salts for making known strength solutions shows that both iron and calcium phosphate, when precipitated with ammonia, 'occlude potash, and that a combination of the two is even more effective in producing occlusion.

LABORATORY OF THE SOUTH CAROLINA EXPERIMENT STATION CLEMSON COLLEGE, S. C.

#### DETERMINATION OF THE VALUE OF AGRICULTURAL LIME

By S. D. CONNER Received May 23, 1918

Three analytical methods are commonly used for determining the value of agricultural limes and limestones.

I—The making of an analysis and calculating the value of the material from the percentages of calcium and magnesium found.

2—The determination of carbon dioxide and calculating the value of the limestone from this alone. Quite a number of devices have been introduced in late years to make it possible to carry out this estimation quickly and easily.

3—The determination of the acid-neutralizing power of the material by digesting in a slight excess of standard acid, then titrating the excess acid with standard alkali. The titration method has been used during the past five years on many samples of limestone, burned lime, hydrated lime, gas lime, marl, shells, various by-products from beet sugar factories, acetylene generators, refuse from water-softening plants, etc. It has in all cases been found very accurate and rapid.

#### TITRATION METHOD

#### The procedure used by the author follows:

Pulverize a sample of the stone in an iron mortar until it feels free from grit. Weigh out exactly one gram and place it in a 250 cc. beaker, cover with a watch glass and introduce, at the lip, without removing the cover, 6 cc. of 4 N hydrochloric acid. When the effervescence nearly ceases add 75 cc. distilled water and boil gently in the covered beaker for 10 or 15 min., in which time the reaction is completed and the carbon dioxide driven off. Cool and titrate to faint pink with N/2sodium hydroxide, using phenolphthalein as indicator.

The results are calculated to the equivalent of calcium carbonate and the acid-neutralizing power

of the limestone is reported in terms of per cent of calcium carbonate. With pure calcium carbonate at one hundred, some magnesites and dolomites will show a calcium carbonate equivalent of over one hundred.

PRECAUTIONS TO BE OBSERVED—It is best to cool the solution before titrating, as phenolphthalein is more sensitive in the cold and also because some limestones contain enough soluble iron to destroy the indicator. This destructive action is very much greater in a hot solution than it is in a cold one. Solutions which give much ferrous hydroxide on neutralization should be titrated slowly and with the addition of new portions of indicator when nearing the end-point.

With materials high in magnesium, such as magnesite, it is advisable to titrate slowly, as the color change of the indicator is slow. If the end-point is passed the solution can be titrated back with a standard acid.

By running a blank determination on the acid it will be found that boiling does not cause appreciable loss of acid and does not materially affect the determination.

#### POT TESTS

Pot tests on two types of acid soil with several calcium and magnesium stones have been conducted. The crops grown were wheat and red clover. Each treatment was conducted in duplicate in paraffined galvanized iron pots  $9^{1}/_{4}$  in. in diameter and 11 in. deep. The pots were subwatered by means of a tube connected to an arch at the bottom of the pot.

Both the wheat and clover were sown February 27, 1917. After germination the seedlings were thinned so that only three plants of wheat and three of clover were left per pot. The pots were weighed at regular intervals and kept at one-half the water holding capacity of the soils throughout the experiment. The wheat was harvested September 1, 1917, and the clover January 15, 1918.

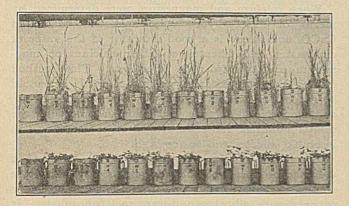


Fig. 1—Pot Tests with Wheat and Clover on Acid Black Sandy Soil, Treated with Various Minerals. See Table II

Two radically different types of acid soils were used in the tests. Soil W is a peaty sand high in organic matter, containing 5.72 per cent ammonia-soluble humus before extracting with dilute HCl and 4.96 per cent humus after extracting with acid. Soil D is a yellow silty clay very low in organic matter, containing 0.73 per cent humus before and 0.70 per cent humus after extraction with acid. These soils were selected because Soil W represents a type predominating in organic acidity and Soil D represents a typical inorganic acid soil with very little organic acidity. In view of the fact that the results obtained on the two types of soil agree very closely it seems logical to conclude that like results would be obtained on other soils of an equal degree of acidity. Both soils used are very acid and it is quite probable that somewhat different relative results would be obtained if similar tests were conducted with soils of slight or medium acidity.

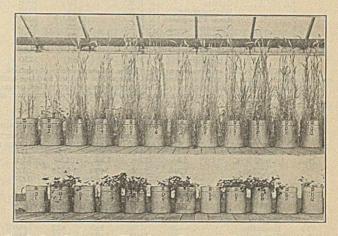


FIG. 2—POT TESTS WITH WHEAT AND CLOVER ON ACID YELLOW SILTY CLAY SOIL TREATED WITH VARIOUS MINERALS. SEE TABLE II

In addition to pure cleavable calcite (calcium carbonate) the following high-grade minerals, pulverized to pass a one-half millimeter sieve, were used to test their values in neutralizing soil acidity and increasing crop growth: Wollastonite (calcium silicate), raw rock phosphate (commercial), gypsum (calcium sulfate), dolomite (calcium magnesium carbonate), magnesite (magnesium carbonate), enstatite (magnesium silicate), serpentine (magnesium silicate).

The comparative test of the different minerals was made in addition to a basic application of nitrogen. phosphate, and potash fertilizer. This basic fertilizer was applied at the following rates per million pounds soil: 91 lbs. ammonium nitrate, one-third applied at the start and the remainder at intervals of two months; 73 lbs. di-ammonium phosphate all at the start; 100 lbs. di-potassium phosphate all at the start. The basic fertilizer was prepared from neutral chemicals of the highest purity free from calcium or magnesium. It is approximately equivalent to a field application of 1000 lbs. per acre of a formula containing 6 per cent N, 8 per cent P2O5, and 8 per cent K<sub>2</sub>O. All treatments were thoroughly mixed with the proper weight of soil before the pots were filled. At the end of the experiment soil samples from each pot were taken the full depth of the pots by means of a soil tube and tested for acidity.

Table I shows the CaO, MgO, and  $CO_2$  in the minerals used, also the calculated calcium carbonate equivalent as determined by three methods.

		-PER CENT	SOLUBLE IN I			EQUIVALEN	
MINERAL	Theoretical Formula	CaO Per cent	MgO Per cent	CO <sub>2</sub> Per cent	By CaO and MgO Per cent	By CO <sub>2</sub> Per cent	By Titration Per cent
Calcite	CaCOa	56.00	0.10	43.65	100.1	99.2	99.5
Wollastonite	CaSiO <sub>3</sub>	38.65	0.12	0.13	68.8	0.3	68.6
Rock Phosphate	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	25.65	0.20	1.20	46.3	2.7	12.3
Gypsum	CaSO4.2H2O	33.25	0.22	0.22	59.3	0.5	0.0
Dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub>	30.40	20.50	47.04	105.6	106.9	106.0
Magnesite	MgCO <sub>3</sub>	0.12	46.20	51.00	115.6	115.9	116.2
Enstatite	MgSiO <sub>3</sub>	0.08	0.28	0.16	0.8	0.4	0.3
Serpentine	Mg3Si2O7.2H2O	0.05	19.11	0.25	47.9	0.6	45.4

#### TABLE II-SOIL ACIDITY AND CROP RETURNS WITH DIFFERENT TREATMENTS IN POT TEST

OIL AFTER CROPPING <sup>2</sup>	AVERAGE VIELDS PER POT
	Wanatah soil Dupont soil
	Wheat Clover Wheat Clover
Lbs. Lbs.	Grams Grams Grams Grams
2460 4000	0.5 0.0 0.7 0.0
20 750	17.0 9.5 10.5 11.0
2800 4125	1.5 3.5 44.0 2.0
400 1750	
20 750	
260 1625	33.5 8.5 65.5 3.0
1780 3500	
1980 3500	
40 750	
20 625	
2260 3500	
1700 2750	21.5 8.5 54.5 3.0
	Dupont soil           H         J           Lbs.         Lbs.           2460         4000           20         750           200         1750           260         1625           1780         3500           1980         3500           400         750           20         625           1780         3500           400         750           20         625           200         3500

<sup>1</sup> (N P K) = 91 lbs, ammonium nitrate, 73 lbs, di-ammonium phosphate, and 100 lbs, di-potassium phosphate per million pounds soil. All minerals were used at rate of 2 tons per million pounds soil, sceept Pot 4 which had one-half quantity of calcite. <sup>3</sup> All acidity figures are in terms of CaCO<sub>3</sub> requirement per million pounds soil. <sup>3</sup> H = By Hopkins potassium nitrate method, U. S. Dept. Agr., Bur. of Chem., Bull. 107 (revised). J=C. H. Jones calcium acetate method, Proc. Of. Agr. Chem., 1914.

TABLE III-SOIL ACIDITY DECREASES AND CROP INCREASES BY TREATMENTS AND SOILS

		DECRI	EASE IN	ACIDITY F	ER 1,000	,000 LBS.	Son	-	A	VERAGE C	CROP INCR	EASES PEL	R Por-	
	Treatment	Wana	tah soil	Dupor	it soil	Average	soils	Wana	atah soil	Dup	ont soil	Averag	e soils	Wheat and
Pot	in addition	H1	T1	H	I	Н	I.	Wheat	Clover	Wheat	Clover	Wheat	Clover	Clover
No.	to N P K	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Grams	Grams	Grams	Grams	Grams	Grams	Grams
4	1/2 Calcite	1240	2250	2400	2375	1320	2312	26.0	4.5	10.5	10.5	18.2	7.5	25.7
5	Calcite	1720	3750	2780	3375	2250	3562	33.5	9.0	21.5	16.5	27.5	12.7	40.2
6	Wollastonite	1580	3500	2540	2500	2060	3000	32.0	5.0	21.0	1.0	26.5	3.0	29.5
7	Rock Phosphate	600	1500	1020	625	810	1062	17.0	5.0	10.5	6.0	13.7	5.5	19.2
8	Gypsum	340	1250	820	625	580	937	0.0	-3.0	6.5	-1.5	3.2	-2.2	1.0
9	Dolomite	1680	4000	2760	3375	2220	3687	33.5	8.0	18.5	18.0	26.0	13.0	39.0
10	Magnesite	1700	4250	2780	3500	2240	3875	32.5	5.0	20.0	14.0	26.2	9.5	35.7
11	Enstatite	-20	750	540	625	260	687	2.0	-0.5	5.5	0.0	3.7	-0.2	3.5
12	Serpentine	600	1500	1100	1375	850	1437	20.0	5.0	10.5	1.0	15.2	3.0	18.2
I = Hopkins potassium nitrate method. I = C. H. Jones calcium acetate method.														

Table II gives the arrangement and treatment of the pots, together with the soil acidities found at the end of the test, also the yields in grams of air-dry wheat (grain and straw) and of clover hay. The widely divergent figures obtained in determining the acidity of the two soils with the various treatments illustrates the fact that the acidity of Soil W is largely organic in nature while the acidity of Soil D is almost all inorganic. The results obtained with the potassium nitrate method are not affected to any great degree by organic acidity, while the results obtained with the calcium acetate method are very largely affected by organic acidity.1

Figs. 1 and 2 show the appearance of the wheat and clover crops on each soil series just before harvesting.

Table III gives the relative decreases in soil acidity for each treatment as shown by the Hopkins potassium nitrate method and by the C. H. Jones calcium acetate method. The relative crop increases over the basic fertilizer treatment, as well as the average wheat increases, the average clover increases, and the total increases of wheat and clover, are shown for each treatment.

Fig. 3 gives the calcium carbonate equivalents of the different minerals used by the titration method in comparison with the relative crop increases and the soil acidity decreases as shown by the Hopkins and Jones methods. The full application of calcite was taken as one hundred in each case. The acid-neu-

1 S. D. Conner, J. Assoc. Off. Agr. Chem., 3 (1917), 139.

tralizing power of the minerals used, as determined by titration, correlates with the crop increases and acidity decreases except in two cases. The high crop yield in the case of the rock phosphate may be partly due to a phosphate action in addition to that of the neutralizing value of the calcium. The relatively lower crop increase with magnesite is probably due to the fact that magnesia has an injurious action under certain conditions.

When calcium and magnesium were determined by means of dilute hydrochloric acid the calculated CaCO<sub>3</sub> equivalent is a good indicator of the value of carbonates and silicates of either calcium or magnesium and of raw rock phosphate. This method fails entirely in the case of calcium sulfate. It should be noted here that if an analysis of the total calcium and magnesium is made, by fusion or otherwise, the results obtained for enstatite or other more or less insoluble silicates will be too high.

The results obtained by means of the CO2 method are in accordance with the crop results only in the case of the carbonates and gypsum. This method fails entirely with silicates and raw rock phosphate. It is only with boiling acid that the CO2 method will indicate the value of magnesite and some dolomitic limestones, as such minerals are not completely dissolved by cold hydrochloric acid. The CO2 method, of course, would not indicate the value of burned or hydrated lime or of many waste products which might be used for correcting soil acidity.

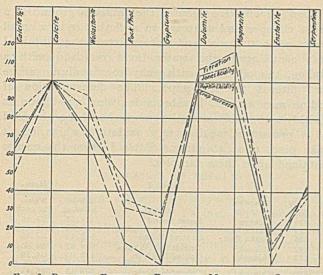


FIG. 3—RELATIVE EFFECT OF DIFFERENT MINERALS AS SHOWN BY AVERAGE INCREASE OF WHEAT AND CLOVER AND DECREASE IN SOIL ACID-ITY BY THE HOPKINS AND JONES METHODS COMPARED WITH ACID-NEUTRAL-IZING POWER OF THE MINERALS DETERMINED BY TITRATION. FULL CALCITE APPLICATION TAKEN AS 100

It is a well-established fact that certain silicates of calcium and magnesium compare favorably with calcium and magnesium carbonates in neutralizing acidity and in their beneficial action upon soils.<sup>1</sup> Dana<sup>2</sup> states that gypsum occurs intermingled with limestone. Clarke<sup>3</sup> says, "Wollastonite is commonly found as a product of contact metamorphism, especially in limestones;" also, "In many localities serpentine is associated with dolomite or dolomitic limestones."

Taking all these factors into consideration it would appear that the acid-neutralizing power of the limestone as determined by titration is the best method to use for determining the value of agricultural limes and limestones.

#### SUMMARY

I—The value of agricultural limes was determined by means of the acid-soluble calcium and magnesium, by means of  $CO_2$  determination with boiling hydrochloric acid, and by digesting in standard acid and titrating the excess acid.

II—Pot cultures on two very acid soils were conducted using calcite, wollastonite, raw rock phosphate, gypsum, dolomite, magnesite, enstatite, and serpentine as correctors of soil acidity.

III-Wheat and clover were grown in each soil and the crop increases reported.

IV—Soil acidity was determined after cropping by means of the Hopkins potassium nitrate method and the C. H. Jones calcium acetate method.

V-Crop increases due to various treatments were obtained in the following order, the highest being placed first: Calcite, dolomite, magnesite, wollastonite, rock phosphate, serpentine, enstatite, and gypsum.

<sup>1</sup> McIntire and Willis, THIS JOURNAL, 6 (1914), 1005; Ames and Schollenberger, Ohio Expt. Sta., Bull. 306 (1916), 385; Cowles, Met. & Chem. Eng., 17 (1917), 664.

<sup>3</sup> Clarke, U. S. Geol. Surv., Bull. 616, 378 and 603.

VI—The treatments decreased the soil acidity in the following order: Magnesite, dolomite, calcite, wollastonite, serpentine, rock phosphate, gypsum, and enstatite.

VII—The results obtained in these experiments 1 indicate that the value of agricultural lime is in accordance with its acid-neutralizing power, rather than with the CaO, MgO, or  $CO_2$  contained, and that the titration method is the most accurate and reliable method for determining the value of agricultural limes.

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#### THE DETERMINATION OF THE HEXABROMIDE AND IODINE NUMBERS OF SALMON OIL AS A MEANS OF IDENTIFYING THE SPECIES OF CANNED SALMON

By H. S. BAILEY AND J. M. JOHNSON Received June 21, 1918

At the suggestion of Mr. H. M. Loomis, formerly of the Bureau of Chemistry, an examination of salmon oils for their chemical and physical characteristics was made in 1915 by L. B. Burnett in this laboratory. His preliminary experiments seemed to indicate that the iodine numbers and hexabromide values would furnish a method of distinguishing between the various salmon species.

We have this year made a further study of oils expressed from canned salmon and believe that the results we have obtained justify the assumption that the oil from different species of salmon have characteristic iodine numbers and hexabromide values. In order to get a good working method for determining the so-called hexabromide value of an oil, we carried out a series of experiments using the different procedures suggested by previous investigators.

#### METHODS OF ANALYSIS

The precipitation of insoluble hexabromides from the ether solution of oils and fatty acids was first accomplished in a qualitative way by K. Hazura.<sup>1</sup> A quantitative method for the determination of the hexabromide value was afterwards worked out by Hehner and Mitchell.<sup>2</sup> This method depends upon the low solubility of the hexabromides in a solution of ether and glacial acetic acid. In their method, the precipitate of hexabromides was brought upon a filter paper, washed with ether, dried and weighed. Procter and Bennett<sup>3</sup> found difficulty with Hehner and Mitchell's method especially with the filtration of the precipitate. They changed the solvent and used carbon tetrachloride instead of ether, finally precipitating with alcohol. However, they did not succeed in getting good results when brominating the glycerides and recommended working with the fatty acids. L. M. Tolman<sup>4</sup> modified Hehner and Mitchell's method, using a centrifuge for separating and washing

1 Monatsh., 7 (1886), 637; 9 (1887), 148.

<sup>&</sup>lt;sup>2</sup> Dana, "Manual of Geology," 234.

<sup>\*</sup> The Analyst, 23 (1898), 310.

<sup>&</sup>lt;sup>3</sup> J. Soc. Chem. Ind., 25 (1906), 798.

<sup>4</sup> This Journal, 1 (1909), 340.

the hexabromides, instead of carrying out these operations on a filter. He also weighed in the same flask in which precipitation took place. Tolman allowed the mixture to stand only 30 min. after precipitation, but Sutcliffe,<sup>1</sup> as a result of his investigations, recommended that after bromination, the mixture stand over night at 11° before filtering and washing the precipitate. He found that it was also necessary to add enough bromine to give a good red color instead of merely a yellowish brown as recommended by previous investigators. Sutcliffe's method was later called in question by Gemmell,<sup>2</sup> but he in . reply<sup>3</sup> demonstrated that if his directions were carefully followed his method could be used with satisfaction.

The procedure finally adopted by us is a combination of the methods of Tolman and Sutcliffe, as follows:

About 1 g. of oil is weighed into a tared weighing tube 1 in. in diameter and 6 in. long, 25 cc. of absolute ether are added, and the mixture cooled in ice water. Next there is added very slowly drop by drop from a small burette a mixture composed of 5 cc. of bromine and 25 cc. of glacial acetic acid. This reagent makes an excellent brominating agent and allows the bromine to be added more uniformly and gradually than when pure bromine is used. Besides, it gives the acetic acid necessary for a proper precipitation of the hexabromides. For most oils about 2 or 3 cc. of the solution are required to produce a deep red color, which is considered indicative of a proper excess of bromine.

After the addition of bromine, the weighing tube is allowed to stand in a refrigerator, temperature under 20° C., over night. Next morning it is cooled in ice water and centrifuged from 2 to 4 min., the solvent is then decanted from the precipitate, 10 cc. of ice-cold absolute ether added, the precipitate stirred up with the ether, cooled in ice water, again centrifuged 2 to 4 min. and the ether decanted off. This washing is repeated twice more and after decanting the final wash ether, the weighing tube is dried in an oven at 100° C. to constant weight, 1/2 hr. usually being sufficient. In the case of salmon oils which gave a very large percentage of hexabromides, a weighed quantity of the oil was mixed with a weighed quantity of a cottonseed oil, which by test had shown no hexabromide precipitate, and the hexabromide value was then determined upon the mixed oil and calculated back to the original salmon oil. This was found necessary as a very bulky hexabromide precipitate could not be readily centrifuged and washed rapidly enough to prevent the solution warming up and dissolving some of the hexabromides. In order to get concordant results with an empirical method of this kind of course every precaution must be taken to work always under exactly the same conditions. After a little experience in the manipulation of this method, it is possible to obtain duplicate determinations which agree within 0.2 per cent with oils having a hexabromide value of 25 to 50.

The iodine number was determined upon a separate portion of each sample by the regular official Hanus method.<sup>4</sup>

#### ANALYSIS OF SALMON OILS

The salmon oils which we examined were obtained from canned salmon furnished us by Dr. E. D. Clark of the Food Research Laboratory and were collected by him from various typical districts on the Pacific Coast in 1916. Enough cans to furnish the necessary

1 The Analyst, 39 (1914), 28.

<sup>2</sup> Ibid., **39** (1914), 297. <sup>3</sup> Ibid., **39** (1914), 388.

4 J. A. O. A. C., [3] 2, Part II, 305.

amount of oil were opened, the contents ground in a meat chopper and squeezed in a cloth bag in a small screw press. The oil and water mixture thus obtained was centrifuged, the water layer removed with a siphon, the oil dried with anhydrous sodium sulfate and filtered through paper. The determination of iodine number and hexabromide value was made as quickly as possible after the sample had been prepared as a precaution against any oxidation which might take place upon standing. Table I gives the results obtained upon these samples.

		TABLE I		Hexa-
O. F. W. No.	VARIETY SALMON	Source	Iodine Number	bromide Value Per cent
611	Sockeye	Puget Sound	141.55	33.36
584	Alaska Red	So. Eastern Alaska	140.72	32.61
586	Alaska Red	Central Alaska	148.10	37.35
587	Chinook	Bristol Bay, Alaska	$126.62 \\ 128.03 \\ 134.48 \\ 129.13 \\ 130.40 \\ 129.06$	24.90
573	Chinook	Columbia River		24.58
577	Chinook	Rogue River (fall)		31.06
579	Chinook	Columbia River		26.45
583	Chinook	Rogue River (spring)		29.52
588	Chinook	Washington Coast		23.86
575	Silverside	Rogue River	166.30	59.31
576	Silverside	Columbia River	161.05	47.82
585	Medium Red	So. Eastern Alaska	166.40	50.91
590	Coho	Washington Coast	155.61	45.98
574	Chum	Columbia River	133.10	27.62
589	Chum	Central Alaska	136.19	30.12
595	Chum	Bristol Bay, Alaska	133.25	27.59
581	Steelhead	Columbia River	141.90	36.22

In the following table are given the figures found for oils extracted with ether from single cans of Puget Sound salmon packed under direction of Mr. R. W. Hilts in 1912-13.

	TAE	LE II	
0. F. W.	VARIETY	Iodine	Hexabromide Value
No.	SALMON	Number	Per cent
613	Coho	152.51	43.07
615	Pink	153.58	40.17
616	Chum	147.75	35.33

The ether in these oils was removed by evaporation on steam bath in a current of carbon dioxide. That ether extracted oils do not differ appreciably in their constants from cold pressed oils is shown by the analyses of two samples given in Table III.

0. F. W.	VARIETY	Iodine Number	Hexabromide Value Per cent
Contraction of the second second second	(cold pressed)	133.10	27.62
	(ether extracted)	135.43	27.91
589 Chum	(cold pressed)	136.19	30.12
	(ether extracted)	141.28	30.23

The original scheme for this study of the salmon oils contemplated the analysis of fresh salmon as well as the canned product. Dr. Clark had individual fish of several different species extracted with ether during the 1916 season and these ether extracts were later sent to Washington. Although the ether was only partially removed from the oils, and they were kept in wellstoppered bottles in the dark until they could be analyzed, there appears to have been a marked change in their composition. It is plainly evident that the figures obtained upon these samples, as shown in Table IV, do not agree with those from the canned fish of the same species.

A Star Stranger	TAI	BLE IV	Hexabromide
0. F. W. No.	VARIETY	Iodine Number	Value Per cent
598	King	139.49	26.83
602 605 603 604	King Silver Chum Chum	67.08 75.99 112.22 71.68	0.44 2.36

It might be assumed that there was a change in the constants of the oil during the cooking incident to the canning operations and that the values for the oil from the fresh fish were the more nearly normal, if the latter were not much lower than the corresponding values for the canned samples. An increase in the hexabromide and iodine values could hardly have been caused by canning as so far as we know any alteration in fish oils due to heat or oxidation always results in a decrease in these constants.

## DISCUSSION OF RESULTS

Five species of salmon (Oncorhynchus)<sup>1</sup> are found in the waters of the north Pacific: (1) Oncorhyncus tschawytscha quinnat, tyee, chinook, spring or king salmon; (2) Oncorhyncus nerka, blueback, red, sukkegh, or sockeye salmon; (3) Oncorhyncus kisutch, silver, coho, white or medium red salmon; (4) Oncorhyncus keta, dog, keta or chum salmon; (5) Oncorhyncus gorbuscha, humpback or pink salmon. With them the fishermen also incorrectly class the steelhead trout, which really belongs to the closely related genus Salmo.

In Table I we have arranged the salmon oils according to these classifications. It is readily seen by reference to that table that the iodine numbers and hexabromide values run fairly close together for the same variety of salmon. O. F. W. 587 was labeled Alaska Red. Our analysis, however, indicated that this was Chinook. After this sample was analyzed, we submitted additional cans of the same lot to Drs. W. C. Kendall and W. T. Bower, of the Bureau of Fisheries, for identification. They, independently of each other and without knowledge of our results, pronounced the sample as Chinook. Therefore, we have classified it accordingly.

A digest of Tables I and II show the following variations:

TABL	E V				
	Iodine Lowest	Numbers Highest			
Red, Sockeye, or Blueback Chinook, King, or Spring Medium Red, Coho, or Silverside Humpback or Pink Chum or Dog	$\begin{array}{r} 140.72 \\ 126.62 \\ 152.51 \\ 153.58 \\ 133.10 \end{array}$	148.10 134.48 166.40 147.75	32.61 23.86 43.07 40.17 27.59	37.35 31.06 59.31 35.33	

The oils, therefore, show a little more characteristic difference in their hexabromide values than in the iodine numbers. In their iodine numbers, chums and reds overlap, and pinks and medium reds overlap, the highest value in the chums being nearly the same as that in the reds. As only one sample of pink salmon was available for analysis, no sharp conclusion can be drawn as to the limits of the values for the oil of this species. Its iodine value would place it with the medium reds, but its hexabromide value is lower than the lowest found for any medium red sample.

If the coho oils are classified separately, and O. F. W. 616, chum salmon, omitted, we have the following limits in these particular samples.

	Iodine	Hexabromide
	Number	Value
Chinook	127-134	23-31
Chum	133-136	28-30
Red	141-148	33-37
Coho	153-156	43-46
Pink	154	40
Medium Red	161-166	48-59

This arrangement gives a much cleaner-cut distinction between the various species, both with reference to the iodine numbers and hexabromide values. The only case of over-lapping of the constants is between the chums and chinooks.

## CONCLUSIONS

r—A new method or perhaps more properly a modification and combination of several methods for the determination of the so-called hexabromide value of fish oils has been worked out, using an acetic acid solution of bromine as the precipitating reagent.

2—Oils expressed from canned salmon, and dried by the addition to them of anhydrous sodium sulfate, after the major portion of the water has been mechanically removed, have practically the same iodine and hexabromide value as the oils extracted with ether, provided proper precautions are taken to prevent oxidation in the extraction.

3—In so far as a definite conclusion can be drawn from the analysis of comparatively few samples, the results obtained seem to indicate that it may be possible to distinguish the variety of canned salmon by a determination of the hexabromide and iodine values of the oil.

OIL, FAT AND WAX LABORATORY BUREAU OF CHEMISTRY U. S. DEPARTMENT OF AGRICULTURE WASHINGTON, D. C.

## COMPOSITION OF THE WATERS OF THE INTER-MOUNTAIN REGION

By J. E. GREAVES AND C. T. HIRST Received April 1, 1918

During the years 1916 and 1917 the chemical department of the Utah Agricultural Experiment Station made several hundred analyses of waters representing 58 streams, the majority of which were extensively used for irrigation purposes. The results obtained are of exceptional interest, for they indicate the great quantitative and qualitative difference in the composition of the irrigation waters. Moreover, they clearly portray the enormous quantities of soluble salts which at times may be carried to soil by water and the great part which waters play in the formation of alkali soil.

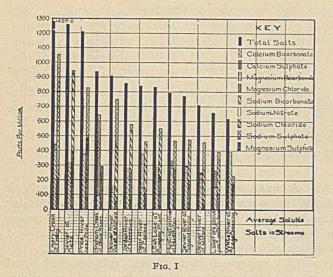
From the majority of streams monthly samples were taken during the irrigation seasons. These were collected according to standard methods in carefully cleaned containers and shipped to the laboratory where the analyses were made as soon as possible and according to the following methods.

## METHODS OF ANALYSIS

TOTAL SOLIDS—Fifty cc. of water were evaporated to dryness on an electric hot plate in 100 cc. beakers, cooled in desiccators, and weighed accurately to the fourth decimal place.

CARBON DIOXIDE-Fifty cc. of water were titrated

<sup>&</sup>lt;sup>1</sup> John N. Cobb, "Pacific Salmon Fisheries," Bureau of Fisheries, U. S. Department of Commerce, 1917, Document No. 839.



against  $N/_{30}$  H<sub>2</sub>SO<sub>4</sub>, using methyl orange as an indicator.

CHLORINE—Determined by Volhard's method, using  $N/_{50}$  AgNO<sub>3</sub>.

CALCIUM—Twice precipitated as calcium oxalate, each time washed, and finally titrated against N/10 KMnO<sub>4</sub>.

MAGNESIUM—The filtrate from the calcium was concentrated, the magnesium precipitated by microcosmic salt and weighed as magnesium pyrophosphate.

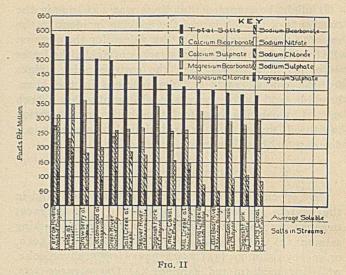
NITRIC NITROGEN—Fifty cc. of water were evaporated to dryness, the residue treated with 2 cc. phenoldisulfonic acid, allowed to stand ten minutes, and then diluted with water. The solution thus obtained was made alkaline with ammonia, and the color compared with a standard solution of potassium nitrate in a Kennicot colorimeter.

The analysis of the water would give the basic and acidic ions in the water, but in reporting the results conventional combinations have been made according to the calculations recommended<sup>1</sup> by the Association of Official Agricultural Chemists. These results are reported as parts per million of water. That is, according to the recommendation the hypothetical combinations are made by calculating the calcium and magnesium to the acid ions in the following order: bicarbonate, sulfate, and chloride. Any remaining acid ions are calculated to sodium.

The results, which are the average of from three to seven analyses made on samples of water taken at different times, are given in Figs. I to IV. The results so presented give us at a glance the total and relative quantities of total soluble salts, non-toxic bicarbonates and calcium sulfate, and toxic chlorides and sulfates.

In so grouping the various streams into the four divisions we do not wish to convey the idea that all in the first group may prove injurious or that all in the second or third group may be used with impunity, but it has been used merely as a convenient method of dividing, although a glance at the tables shows quite a marked qualitative and quantitative difference in the various groups.

1 J. A. O. A. C., [4] 1, Part II, 51.



All of the waters, the analyses of which are listed in Fig. I, are high in soluble salts.

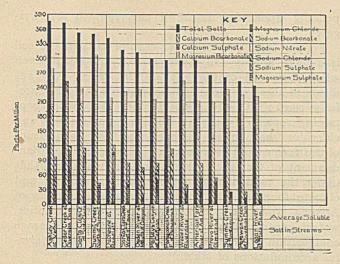
It is, however, questionable whether any of them are high enough in saline constituents to destroy plants at the present concentration. But the magnitude of the problems which confront the users of such waters is made clear by the following consideration: one acre-foot of the Sevier River water would carry to the soil 3581 lbs. of soluble salts which in 20 such irrigations would reach the enormous sum of 71,628 lbs., 75 per cent of which consists of toxic salts. This in itself, if it be allowed to concentrate in the surface foot, would be sufficient to render the soil sterile. White River, which is lower in soluble salts than any of the others in this group, would carry to the soil in every acre-foot 1502 lbs. of salts, or in 20 such applications there would be added to the soil over 15 tons of soluble salts.

Moreover, the water of the Sevier contains comparatively small quantities of calcium and magnesium bicarbonates and enormous quantities of the chlorides and sulfates. The unbalanced condition of the salts in Beaver River water makes it even more dangerous than are the Sevier or Price River waters. It is important to note that in all of these streams, with the exception of the White River, the toxic chlorides and sulfates greatly predominate over the bicarbonates.

While the composition of these waters do not vary greatly from year to year, there is a great variation within one season. As a general rule, the concentration of the salts in the water increases with the season. The Sevier water is only two-thirds as concentrated during June as it is during September.

The fourteen streams listed in Fig. II are quite different in composition from those previously considered.

With the exception of Ferron, Uinta, and Green Rivers, the non-toxic bicarbonates predominate, and even in these three streams there are large quantities of calcium and magnesium bicarbonates which would tend to neutralize the toxicity of the other salts, although the problem confronting the users of these waters is not nearly so complex as is the problem



#### FIG. III

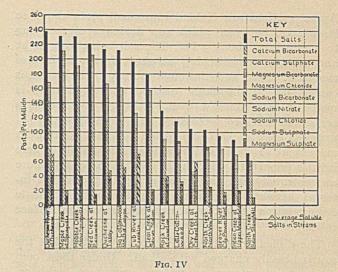
which confronts the users of the waters listed in Fig. I. None of these waters contain sufficient salts to be of injury to plant life, but the tendency to accumulate in the soil is impressed upon the individual in passing over districts in which the waters have been injudiciously used.

The streams which are listed in Fig. III contain between 340 and 380 p. p. m. of soluble salts and in every case the non-toxic bicarbonate greatly predominates. In not one case do the toxic salts reach 150 p. p. m. and in most cases the quantity present is far below this amount.

These waters, if intelligently used on land, with even fair drainage and not already filled with alkali, should give no trouble. On the contrary, the quantity and quality of the soluble constituents act as plant stimulants. In short, this condition is found to occur with many of even the high alkaline waters and the injury comes only after there is a concentration of the soluble salts within the soil.

All of the waters which are listed in Fig. IV contain less than 180 p. p. m. of soluble salts and in every case the toxic salts make up only a small fraction of the total salts.

Sevier River and its tributary, Clear Creek, present an interesting study. Clear Creek is a stream containing only a small amount of soluble salts and over 76 per cent of this in the form of the non-toxic bicarbonates. But after flowing about 50 miles through a district rich in soluble salts, receiving seepage and being concentrated by evaporation, its nature has been so changed that by the time it reaches Sigurd Bridge, at Sigurd, it is a strongly saline water. In flowing from Sigurd to the out-take of the Delta Land and Water Company's canal there is a decrease in common salt, but an increase of over 100 per cent in the equally noxious sulfates. In flowing from Clear Creek to Sigurd Bridge this stream has gained over 400 per cent in soluble salts and the per cent of non-toxic bicarbonates in the water has decreased from 76 per cent to less than 35 per cent of the total. Moreover, by the time the water reaches the Delta Land and Water Company's canal the salts have in-



creased over 600 per cent, with only 25 per cent of them in the form of the calcium and magnesium bicarbonate. We therefore have the transformation from a good carbonated water to a strongly saline sulfate water which presents a tremendous problem to the water user.

It is hard to place a limit upon the quantity of alkali which may be in a water and the water still be used for irrigation purposes, for it varies greatly with a number of factors, chief among which are the kind and quantity of alkali and the soil; the method of irrigation and the quantity of water applied; the physical nature of the soil as to whether sandy or clayey and whether drained or water-logged.

It is generally conceded that sodium carbonate is more injurious than the chlorides or sulfates. Practically all of the waters examined are very low in sodium carbonate, but we must not lose sight of the fact that sodium sulfate or sodium chloride, in the presence of large quantities of decaying organic matter which liberates carbon dioxide, may be readily transformed in the soil into the more harmful carbonate. Moreover, water which contains sodium carbonate, if used on soils containing large quantities of gypsum, will be no more detrimental than if it contained an equal amount of sulfate; for the gypsum would readily convert the carbonate into the less toxic sulfate.

Moreover, as we have seen from the given results, a stream may be comparatively free from alkali at one season while at another it may be heavily charged with alkali. The melting of snow in the mountainous regions usually has the effect of freshening the water, while local rains often have the opposite effect. Drainage water, especially from alkali soils, greatly increases the alkali content of the water. Many of the cases in which large increases of alkali are noted in the water during the later irrigation season must be attributed to this factor.

With good natural drainage a more highly concentrated water may be used than where drainage is poor. For instance, in the Algerian Oases, where alkaline waters are used, the conditions are as follows: "The Arabs' gardens are divided into small plots about 20 ft. square, between which run drainage ditches dug to a depth of about 3 ft. The soil being very light and sandy, this ditching at short intervals insures the most rapid and thorough drainage. Irrigation is carried on by the check method and application is made at least once a week, although two wettings are often deemed necessary. A large quantity of water is used at each irrigation. Thus a continuous movement of water downward is maintained. There is little opportunity for the soil water to become more concentrated than the water as applied, and the interval between irrigations being so short but little accumulation of salt from evaporation at the surface takes place."

The difficulty here is added to by the fact that the soil is heavily charged with alkali. Under these conditions such plants as melons, tomatoes, cabbage, pepper, figs, and pomegranates do well. In this work by Means<sup>1</sup> the water used was all artesian water.

Where the soil is a clay loam, heavy adobe or soils with hard pan or poor sub-drainage, entirely different methods must be employed, for the salt would tend to accumulate near the surface and soon become injurious to plants. In soils such as named, every effort must be made to conserve the soil moisture and in this way cut down on the quantity of water added to the soil and with it the alkali salt. It is a fact that often better crops can be produced with r5 in. of irrigation water than with more.

Furthermore, there may be cases in which, because of the physical and chemical composition of the soil, together with the alkali content of the water, the crop must be selected with this fact in view. For instance, sweet or Egyptian clover may be irrigated with water of such a high saline content that it would be fatal to other crops. Old alfalfa is much more resistant to alkali than is young alfalfa.

A soil which is heavily charged with soluble salts may often be tilled if care be exercised in the use of the irrigation water, but when we have such a soil and have to use on it a highly saline water, the problem becomes complex.

Although the use of a saline water on any soil is a problem which must be solved independently in each locality, taking into consideration the saline content of the water, the quantity and nature of alkali in the soil, and the physical conditions of the soil, yet there are certain standards which have been laid down which are valuable guides. Hilgard<sup>2</sup> considers that the extreme limits of mineral content usually assigned for potable waters, viz., 40 grains per gal. (571.2 p. p. m.), also applies to irrigation waters. Should it happen that all or almost all of this were gypsum and Epsom salt, only a large excess of the latter would constitute a bar to irrigation, while, on the contrary, if a large proportion of the solids consists of sodium carbonate or common salt, even a much smaller proportion of salt might preclude its regular use, de-

<sup>1</sup> U. S. Department of Agriculture, Bureau of Soils, *Circular* 10.

<sup>2</sup> California Experiment Station, Bulletin 128.

pending upon the nature of the soil to be irrigated.

Forbes<sup>1</sup> feels that 0.25 per cent of salts in the soil is a more or less dangerous quantity of alkali, even when composed of the less harmful salts. Any addition of alkali in the irrigation waters should be carefully controlled. He states further that water containing 1000 to 1500 p. p. m. of salts as sulfates and chlorides has often embarrassed the agriculture of the farmer and in some cases it has led to the abandonment of farms. Forbes therefore considers "that under the conditions of water supply, drainage, and climate found in the principal irrigated districts of Arizona and with prevailing agricultural practice, waters containing 1000 p. p. m. of salts of average composition are liable to cause in a few years harmful accumulations of alkali."

The Bureau of Soils<sup>2</sup> states that 5000 p. p. m. of soluble salts when added to the Pecos Valley soils may be taken as the extreme limit of endurance by plants, while 250 to 300 marks the danger zone; however, in this case about 50 per cent of these salts are harmful. At Carlsbad about 300 p. p. m. marks the limit of safety.

Means,<sup>3</sup> however, claims that the amount of alkali salts permissible in irrigation water has been underestimated by American writers, and calls attention to the fact that the Arabs in Sahara, Africa, use irrigation water containing over 800 parts per 100,000, more than one-half of which is sodium chloride. He also quotes from an earlier publication: "The limit of endurance for most cultivated plants in a water solution is about 1 per cent, or 1000 parts of the readily soluble salts in 100,000 parts of water."

There is considerable truth in Means' contentions, for many of the early workers on soil alkali failed to take into consideration the effect of balanced solutions on plants and the antagonistic action of one salt to the other.

Viewed in the light of Hilgard's interpretation, we find only thirteen streams the alkali content of which is dangerous, or, if interpreted in the light of Forbes' experience, only two, but according to the work of the Bureau of Soils none should be condemned.

But the fact which must be borne in mind is that even though plants may tolerate large quantities of alkalies in solution if they be in a balanced condition, the great danger comes from the accumulation of the salts in the soil from their continual application. Many saline waters when first applied to a soil may furnish nutrient to the plant and actually stimulate plant growth, but later, due to their accumulation within the soil, have an opposite effect. Hence, users of saline waters must never lose sight of the fact that these waters, if injudiciously used, may be a very potent factor in ruining valuable land.

UTAH AGRICULTURAL COLLEGE LOGAN, UTAH

<sup>1</sup> Arizona Experiment Station, Bullelin 44.

<sup>&</sup>lt;sup>2</sup> Report, 64, page 19.

<sup>&</sup>lt;sup>3</sup> U. S. Department of Agriculture, Bureau of Soils, Circular 10.

## ON CONSTITUENTS OF OIL OF CASSIA-II

By FRANCIS D. DODGE Received June 13, 1918

The examination by the writer and A. E. Sherndal<sup>1</sup> of the alkali-soluble portion of oil of cassia showed the presence of several compounds not hitherto recognized as constituents of the oil. More recently the writer has had occasion to make a further study of this oil, and especially of the aldehyde constituents.

Two samples were examined: one, A, a redistilled oil made in this laboratory from apparently pure commercial oil; the other, B, a commercial U. S. P. oil. The results of the preliminary tests were as follows:

	A	B
Sp. gr. at 25°	1.0528	1.0514
Aldehyde (by vol.)	88 per cent	80 per cent
Rotation	Slightly +	Slightly +
Rosin test	Negative	Negative

One pound of each of the samples was shaken with sufficiently strong sodium bisulfite solution to ensure complete extraction of the aldehydes, the reagent being added in portions of about one pound, waiting after each addition until the crystalline compound had completely redissolved. About 5 lbs. of bisulfite were required for each lot, and when the supernatant oil was found to be free from aldehyde the aqueous solution was separated, and heated on the water bath for several hours to ensure the conversion of the bisulfite compound into the more stable sulfonate. On cooling, the solution was filtered to remove traces of oil. This solution had a slight acid reaction; a portion made alkaline with sodium carbonate became slightly turbid, and showed by odor the presence of aldehyde other than cinnamic, the latter not being liberated by soda.

The entire solution was accordingly made strongly alkaline with sodium carbonate, and extracted with ether. The ether solution was washed with N sodium hydroxide to remove salicylic aldehyde, and then with strong bisulfite to separate other aldehydes. From the alkaline solution the salicylic aldehyde was obtained by acidifying and extraction with ether, and the other aldehydes similarly by neutralizing the bisulfite, and treating with ether. The first ether solution, after treatment with bisulfite, left a small residue of the non-aldehyde portion of the oil, which had remained dissolved in the original bisulfite solution. The results on the two samples were:

	A	В
Original	453 g.	453 g.
Non-aldehyde	About 50 g.	About 80 g.
Salicylic aldehyde	0.985 g.	1.110 g.
Other aldehydes	3.850 g.	4.860 g.
Cinnamic aldehyde	Not recovered	

The small portion of saturated aldehydes thus obtained was, in each case, a heavy, slightly yellow liquid with strong odor of benzaldehyde. That it was not entirely the latter was shown by the behavior with bisulfite solution, in which the aldehyde mixture was completely soluble with evolution of heat, but with only a slight formation of crystals on standing. Benzaldehyde under similar conditions is immediately converted into a crystalline mass. On exposure to the air, the aldehyde mixture oxidized readily, but not

<sup>1</sup> THIS JOURNAL, 7 (1915), 1055.

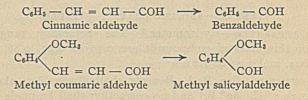
completely to a crystalline acid, melting at 91-93°, which was found by the usual tests to be impure benzoic acid.

A small portion oxidized by permanganate gave an acid which, after crystallization from benzene, melted at 120°, and was evidently benzoic acid. This suggested the possibility of the presence of hydrocinnamic aldehyde, and with the view of limiting the oxidation to the aldehyde group, another portion was oxidized with hydrogen peroxide as follows:

3 g. aldehyde mixture were treated with 30 cc. official peroxide, with a few drops of ferric chloride solution, keeping the mixture slightly alkaline with sodium hydroxide, and adding peroxide until all the aldehyde was in solution. The temperature was kept at 30 to 50°, with frequent agitation. At the end a distinct odor of anisol was noted, which proved significant. Finally the alkaline solution was filtered and concentrated to about 20 g. On acidifying, a crystalline acid mixture, melting below 100°, was precipitated. The characteristic odor of hydrocinnamic acid was not observed, and a separation of the acids by recrystallization from water was not successful.

For further information as to the nature of the aldehydes present, a portion was converted into oxime. One gram aldehyde with one gram hydroxylamine hydrochloride and 33 cc. N/2 alcoholic potassium hydroxide was allowed to stand 3 days, heated to 70° for 3 hrs., neutralized with HCl, diluted to 100 cc., and extracted with ether. On evaporation of the ether solution, long white needles were deposited, which, after pressing and drying, amounted to 0.35 g., and melted at 90° (corr.).

It seemed probable that this oxime might be the oxime of hydrocinnamic aldehyde (m. p.  $93-94^{\circ}$ ), or, more likely, the oxime of methyl salicylic aldehyde (m. p.  $92^{\circ}$ ). The occurrence of the latter could in fact almost be assumed as an oxidation product of the methyl ortho-coumaric aldehyde already noted as a constituent of the oil by Bertram.<sup>1</sup> A similar reaction would explain the occurrence of benzaldehyde.



The occurrence of anisol as an oxidation product would also find an obvious explanation:

$$C_{6}H_{4} \underbrace{OCH_{3}}_{COH} + O = C_{6}H_{5} - OCH_{3} + CO_{2}$$
  
Methyl salicylaidehyde Anisol

To identify the oxime, a portion was converted into nitrile by treatment with acetic anhydride, and the nitrile saponified with alcoholic potassium hydroxide. The reaction, however, did not appear to be smooth; an oily acid was obtained and the result was inconclusive. The conversion into the corresponding acid was, however, attained by the direct oxidation of the oxime with permanganate, a method apparently not previously suggested for this purpose, but which seems

1 J. prakt. Chem., [2] 51, 316.

to be applicable in cases in which the acid formed is comparatively stable toward the reagent.

0.231 g. oxime, dissolved in a few drops of methyl alcohol, was mixed with 2 cc. N/2 potassium hydroxide, and 5 per cent permanganate added gradually until no further oxidation took place. The manganese oxide was then dissolved by sufficient sulfurous acid, the mixture strongly acidified, and the acid taken out with ether. 0.145 g. acid was obtained, which, as it was still contaminated with an oily impurity, was again treated in the same way with permanganate. The acid solution was not extracted with ether, but was allowed to evaporate. After a few days, the greater part of the acid had separated in two large, well-formed prismatic crystals, apparently monoclinic, melting at 89° (corr.), and evidently methyl salicylic acid. A careful comparison with the synthetic acid showed the identity of the preparations, both crystallizing from alcohol in distinct characteristic prisms, showing under the microscope oblique extinction, and a  $\beta$ -angle of about 49°, as described by Graebe.<sup>1</sup>

## EXAMINATION OF THE NON-ALDEHYDE SECTION

The portions of the oil insoluble in bisulfite showed the following properties:

	Α	B	
Sp. gr. at 25°	. 1.020	0.9966	
Rotation	. +0.50°	+0.75°	
Acid value	. 4.0	6.0	
Saponification value	170.0	110.0	
Calc. as cinnamyl acetate	. 53.4 per cent	34.5 per cent	

For further light on the composition of this section, 38 g. of non-aldehyde A were saponified and distilled with steam. About 12 cc. of light oil were obtained, the greater part of the alcoholic product remaining dissolved in the aqueous distillate. To remove alcohols, the oil was washed with 50 per cent resorcin solution, which left a residue of 6.25 cc. light oil, very insoluble in alcohol, and almost unattacked by permanganate. This, in fact, appeared to be a petroleum section, evidently due to an adulteration of the crude oil.

The aqueous distillate, on ether extraction, yielded a small amount of heavy oil, which gave benzaldehyde on oxidation with permanganate, and was probably, in part at least, cinnamyl alcohol. The alkaline residue from the distillation was found to contain acetic and cinnamic acids, and the liquid acid with fruity odor, previously noted.

A comparatively large amount of resin was formed in the saponification, the cause of which remains unexplained.

To conclude, oil of cassia has been found to contain the following compounds:

Previously known:	Cinnamic aldehyde, 75 to 90 per cent Cinnamyl acetate
	Phenyl propyl acetate (?)
	Methyl ortho-coumaric aldehyde
Found by the writer	
and Sherndal:	Salicylic aldehyde, 0.1 to 0.2 per cent
	Coumarin
	Benzoic acid
	Salicylic acid
and the second second second second	Liquid acid of fruity odor
Found by the writer:	Benzaldehyde
Found by the writer.	Methyl salicylaldehyde
	Menyr sancyraidenyde
LABORATORY OF THE	Dodge and Olcott Company

BAYONNE, NEW JERSEY

# LABORATORY AND PLANT

## METHODS OF ANALYSIS USED IN THE COAL-TAR INDUSTRY. IV-BENZOLS AND LIGHT OIL

By J. M. WEISS

Received October 24, 1918

BENZOLS

#### TEST E2-SPECIFIC GRAVITY (SPINDLE)

APPARATUS—Hydrometer.<sup>2</sup> The necessary ranges for this class of compounds are 0.79 to 0.87, 0.86 to 0.94, and 0.93 to 1.01.

METHOD—See B4.<sup>3</sup> Benzols shall always be taken at  $15.5^{\circ}$  C. (60° F.) and no correction shall be made of a reading taken at a different temperature.

NOTE—As under B4.

### TEST E3-SPECIFIC GRAVITY (WESTPHAL)

All matter as to apparatus, method, precautions, and notes as given under H4<sup>4</sup> apply to this test on these materials.

SPECIAL NOTE—This method is the reference method for benzols and must be used in all cases where accuracy is required as in cases of dispute or check testing.

## TEST E4-DISTILLATION OF PURE PRODUCTS

APPARATUS—Flask: The distillation flask shall be a 200 cc. side neck distilling flask having the following dimensions:

<sup>2</sup> See Fig. II, Paper I, THIS JOURNAL, 10 (1918), 735.

<sup>8</sup> THIS JOURNAL, **10** (1918), 735.

4 Ibid., 10 (1918), 911.

Diameter of bulb	73 mm. (2.881 in.)
Outside diameter of neck	24 mm. (0.945 in.)
Inside diameter of neck	21 mm. (0.826 in.)
Length of neck	105 mm. (4.134 in.)
Inside diameter of side tube	5 mm. (0.197 in.)
Length of side tube	127 mm. (5.000 in.)
Side tube joined to neck above the base of	
the neck	52 mm. (2.047 in.)

The side tube shall be set so that the smaller angle where it joins the neck is  $75^{\circ}$ .

The allowable variation from the above dimensions shall be not more than 5 per cent. See Fig. XVI.

Thermometer: This shall be graduated from  $70^{\circ}$  to  $120^{\circ}$  C. at intervals of  $0.2^{\circ}$  C. It shall be made of a suitable quality of glass so as not to change its reading under conditions of use. It shall be provided with an expansion chamber, and a ring at the top for attaching tags. It shall conform to the following dimensions:

Total length	Not over 305 mm.
Bulb length	Not over 20 mm.
70° mark to bottom of bulb	
Graduations per inch	Not over 35 mm.
Stem diameter	5 to 7 mm.
Bulb diameter	5 to 7 mm.
Stem diameter	5 to 7 mm.

The thermometer shall be accurate to  $0.2^{\circ}$  C. at total immersion and shall be compared before use with a similar thermometer calibrated at full immersion by the Bureau of Standards, and proper correction applied.

It is preferable that this instrument shall not have

<sup>1</sup> Ann., 139, 137.

a supplementary bulb situated between the lowest graduation and the main mercury reservoir. However, if such a chamber is present, its lowest point shall be not more than I mm. above the top of the main reservoir.

Condenser: The distillate shall be condensed in a straight tube of 1/2 in. internal diameter and 24 in. in length, set at an inclination of 75° to the vertical. At least 15 in. of tube shall be cooled with cold water in a trough condenser.

Burner: The heating flame shall be derived from a Bunsen burner and the entire flame shall be blue.

Cylinder: An ordinary 100 cc. cylinder, graduated at intervals of 1 cc., shall be used for the receiver. Graduations must be clear cut and distinct. The graduate shall be approximately 1 in. in diameter. The mark for each 10 cc. shall be longer than the intermediate markings and shall be plainly numbered.

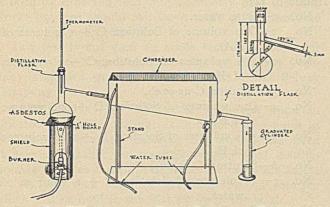


FIG. XVI-ASSEMBLY OF BENZOL DISTILLATION TEST

Assembly of Apparatus: Shown in Fig XVI. The flask shall be supported on a sheet of 1/8-in. asbestos board, 6 in.  $\times$  6 in., with a hole in the center 1 in. in diameter. The asbestos board shall be supported on a circular metal shield enclosing the Bunsen flame. The flask shall be so placed that the vapor tube will extend at least 2 in. into the condenser tube.

The thermometer shall be held in the neck of the distillation flask by means of a cork stopper in such a position that the top of the bulb shall be opposite the lower side of the side tube and central in the neck of the flask.

METHOD—The sample to be tested shall be poured into a 100 cc. graduated cylinder and 100 cc. of the material shall be carefully measured and transferred to the distilling flask. The flask shall be put in connection with the condenser and the thermometer introduced through a tightly fitting cork. The graduated cylinder which was used to measure the oil shall not be rinsed out but shall be placed under the lower end of the condenser tube to catch the distillate. The flask shall be heated up slowly, especially after ebullition has begun, so as to allow the mercury column of the thermometer to become fully expanded before the first drop distils off. The flame shall then be turned up and the distillation conducted at the rate of 5 cc. per min. (2 drops per sec.). This rate must be exact. The distillation shall be continued to dryness. The total yield of distillate shall not be less than 95 per cent.

A temperature reading shall be taken when the first drop of distillate falls into the receiving cylinder. Additional temperature readings shall be taken when 5 per cent and 95 per cent of distillate have distilled over. A final reading shall be taken of the "dry" point, which is the point at which liquid just disappears from the bottom of the flask.

PRECAUTIONS—Care must be taken to quickly remove the burner as the last bubble is evaporated, otherwise, too high a dry point may be produced by superheating.

NOTES—The method given applies to pure benzol and pure toluol.

The specifications for pure benzol and pure toluol require that distillation from first drop to dry shall be complete within a 2° C. range and, further, that the true boiling point of the product in question shall lie within that range.

To be sure that the true boiling point is strictly within this range it will be necessary, of course, to correct the observed temperature readings for variations from the standard thermometer, both for inaccuracy and for stem immersion; also correction should be made for differences in barometric pressure.

The barometric correction factors for each mm. of difference are as follows, these factors being applied directly as the difference in the barometric pressure may be greater or less than 760 mm.

Benzol	0.043°
Toluol	0.047°
Xylol	0.053°

It is not necessary in ordinary works practice to require the chemist to apply these corrections to each test. For instance, if the material is one which boils entirely within a  $2^{\circ}$  range, around, say, from  $77^{\circ}$  to  $81^{\circ}$  C., when the corrections are applied the results will all fall within a similar  $2^{\circ}$  range. The same applies to a  $2^{\circ}$  range between  $108^{\circ}$  and  $112^{\circ}$  C.

It is recommended, however, that such corrections be applied when the sample is to be checked against results obtained by another investigator, and in reporting results in such a case, a notation should be made to the effect that these results have been corrected for the variations mentioned.

An examination of all available literature on such subjects will show that the authorities vary materially in their report of findings of the true boiling points of benzol, toluol and the three xylol isomers. The following figures, however, are considered sufficiently accurate for all commercial practice.

Benzol	80.2° C.
Toluol	110.4° C.
Para-xylol	137.5° C.
Meta-xylol	138.5° C.
Ortho-xylol	142.3° C.

The emergent stem corrections should be made as follows:

- Let C = Number of degrees centigrade to be added to the observed temperature.
  - N = Number of degrees of the stem exposed.T = Average temperature of the bulb.
  - t = Average temperature of the bulb. t = Average temperature of the stem.
  - K = Correction factor for the thermometer, i. e., the difference between the coefficients of expansion of mercury and glass.

Then $C = KN(T-t)$ .	
EXAMPLE.	All a call to all the second
Observed temperature	= 80° C.
Stem temperature	= 25° C.
Degrees emerging (from top of flask to 80° C.)-	= 15° C.
Thermometer coefficient	= 0.000154
80° C. — 25° C.	= 55° C.
15° × 55° × 0.000154	$= 0.12787 = 0.13^{\circ}$ C.
Temperature corrected for emergent stem	= 80.13° C.

#### TEST E5-DISTILLATION OF COMMERCIAL BENZOLS

APPARATUS—Exactly as given for E4 with the following exceptions: (1) The thermometer shall be a standard  $0^{\circ}$  to  $400^{\circ}$  C. thermometer (see C9)<sup>1</sup>; (2) For materials boiling substantially below 145° C. a 1-in. hole shall be used in the asbestos board on which the flask is supported. For materials boiling substantially above 145° C. a 2-in. hole shall be used.

METHOD—The distillation shall be conducted exactly as given under E4.

"Special Specification Xylol" shall be read first drop, 5 per cent off, 50 per cent off, 95 per cent off, and dry, as under E4.

All other materials, except "Pure Xylol," shall be read at first drop, and then volume readings taken at every even 5° C. up to the dry point, thus:

Deg. C.	Per cent
77	1st drop
80 .	10
80 85	65
90 95	78
	83
100	90
105	98
, 108	Dry

"Pure Xylol" shall be read, first drop, every 1° C., and dry.

PRECAUTIONS-Same as under E4.

NOTES—In light fractions it is well also to determine loss by pouring the liquid that recondenses in the flask into the graduated cylinder and noting the total volume. The difference between the reading and roo gives the approximate result for "loss."

In some cases on the xylols where special accuracy is required a thermometer graduated from  $110^{\circ}$  to  $160^{\circ}$  C. in 0.2° C. intervals is used. This is not necessary for ordinary practice. The specification, except for scale range, is the same as for the  $70^{\circ}$  to  $120^{\circ}$ thermometer given under E4.

This test, as well as E4, has been compiled from our experience and also from matter given in the Gas Chemists' Handbook, page 180, the standard method for distillation of paint thinners (A. S. T. M., D-28-17), and the article<sup>2</sup> by F. W. Sperr, Jr., of the H. Koppers Co.

## TEST E6-SULFURIC ACID WASH

APPARATUS—Standards: The set of color standards against which wash tests shall be compared shall consist of fifteen bottles (French square flint glass, glass stoppered, one ounce capacity) each containing

<sup>1</sup> THIS JOURNAL, **10** (1918), 819. <sup>2</sup> Met. & Chem. Eng., Nov. 15, 1917, p. 586. one of the colored solutions made up as given below, the bottle being sealed.

For making up the standards the following basic solutions shall be used:

- A-59.4965 g. CoCl<sub>2</sub>.6H<sub>2</sub>O (nickel-free) made up to 1000 cc. with a mixture of 25 cc. 31 per cent HCl and 975 cc. H<sub>2</sub>O.
- B—45.054 g. FeCl<sub>3</sub>.6H<sub>2</sub>O made up to 1000 cc. with a mixture of 25 cc. 31 per cent HCl and 975 cc. H<sub>2</sub>O.
- C—3.5 volumes of Solution A +  $_{3}6.5$  vol. Solution B +  $_{9}0$  vol. of H<sub>2</sub>O.
- D-3.5 volumes of Solution A + 36.5 volumes of Solution B. (No water is added.)
- E-Solution of K<sub>2</sub>CrO<sub>4</sub> saturated at 21° C.
- F—One volume of a solution of  $K_2Cr_2O_7$  saturated at 21° C. + one volume of  $H_2O$ .

As standard color solutions to be used for comparison the following shall be made up and numbered from o to 14:

- No. o-Pure water.
- No. I—One volume of Solution C + I volume of  $H_2O$ .
- No.  $2-5^{1/2}$  volumes of Solution C + 2 volumes of H<sub>2</sub>O.
- No. 3-Solution C as such.
- No. 4—One volume of Solution D + one volume of  $H_2O$ .
- No.  $5-5^{1/2}$  volumes of Solution D + two volumes of H<sub>2</sub>O.
- No. 6-Solution D as such.
- No. 7-5 volumes of Solution E + 2 volumes of water.
- No. 8-Solution E as such.
- No. 9-7 volumes of Solution E + 1/2 volume of Solution F.
- No. 10 $-6^{1/2}$  volumes of Solution E + one volume of Solution F.
- No. 11— $5^{1/2}$  volumes of Solution E + two volumes of Solution F.
- No. 12—One volume of Solution E + one volume of Solution F.
- No. 13—Two volumes of Solution E + 5 volumes of Solution F.
- No. 14—Solution F as such.

These standard solutions shall, in all cases, remain stoppered and sealed to prevent evaporation.

Test Bottles: These shall be one-ounce, French square, glass-stoppered, flint glass bottles identical in every respect with those containing the standard solutions. (A suitable bottle is shown in the Whitall Tatum 1910 catalogue, p. 21.)

METHOD—7 cc. of 96 per cent C. P. sulfuric acid shall first be placed in a test bottle and approximately 21 cc. of the material to be tested shall be added. The bottle after being stoppered shall be thoroughly and vigorously shaken for 15 to 20 sec. and allowed to stand for the specified time. (See Notes.)

The resulting color of the acid layer shall be compared with the set of standards and the number of the bottle in the standard set corresponding to the test bottle shall be noted. PRECAUTIONS—If the color of the acid layer is not uniform, it should be carefully mixed by slowly inverting bottle once or twice.

96 per cent sulfuric acid must be used. Some C. P. acid obtained is only 94 per cent and care must be taken to see that the strength is of the proper degree.

NOTES—In pure benzol and pure toluol testing the benzol or toluol layer must remain white, and the color of the acid layer, after standing 15 min., must not be darker than No. 4.

For 90 per cent benzol and all grades of benzol and toluol other than pure, the benzol or toluol layer must remain white, and the color of the acid layer after standing 15 min. must not be darker than No. 6.

For solvent naphtha the acid layer color only is noted, and after standing 5 min. it must not be darker than No. 14.

It is well to note that the above schedule shows the limit of color allowable in the sales specifications, and it is to be expected that to consistently pass the test, works practice should call for a limit of at least one number lighter in each case.

This test is not used on crude benzols. The color standards are a modification of the old Barrett Company standard practice made by the Semet-Solvay Company.

SPECIAL NOTE—In making the wash test upon an agitator charge, this being recommended as a guide in determining whether material in question has been sufficiently washed to warrant making final distillation, it is necessary to first make the sample alkaline by shaking with some of the caustic soda solution which will be used in the factory upon the wash.

This is best carried out in a separatory funnel. After shaking, the mixture is allowed to settle and the soda solution drawn off as thoroughly as possible. 100 cc. of the neutralized oil are then measured in a graduated cylinder and transferred to a 200 cc. distilling flask.

No thermometer need be used in this distillation, but care should be taken to make the distillation through a condenser which has been used for pure products, so that the distillate may not be contaminated in the condenser.

The first 5 cc. distilled off are rejected. Then 70 cc. are distilled off and caught in a clean graduated cylinder. The cylinder which was used to measure the material into the flask should not be used for this, as it would tend to contaminate the distillate. The 70 cc. of distillate thus caught are filtered through a clean, dry, white filter, and tested for wash as described.

If the resulting test is entirely satisfactory, the factory alkali wash and result in distillation may be safely relied on.

## TEST E7-CARBON BISULFIDE

APPARATUS—Erlenmeyer flask, rough balance, burette, separatory funnel 250 cc. capacity.

REAGENTS—Solution of alcoholic caustic potash, prepared by dissolving 110 g. of potassium hydroxide in 900 g. of absolute alcohol. Standard solution of copper sulfate (1 cc. equivalent to 0.0075 g. CS<sub>2</sub>), prepared by dissolving 12.475 g. of CuSO<sub>4</sub>.5H<sub>2</sub>O in one liter of distilled water. Potassium ferrocyanide solution. Acetic acid solution.

METHOD-Exactly 50 g. of the benzol to be tested shall be weighed into an Erlenmeyer flask, mixed well with 50 g. of alcoholic potassium hydroxide solution, the flask stoppered and the mixture allowed to stand for 5 or 6 hrs. at the ordinary temperature. The carbon bisulfide by this treatment is converted to potassium xanthate. The mixture shall then be shaken up with about 100 cc. of water and the aqueous layer separated from the benzol. This washing shall be repeated several times with 30 cc. portions of water, adding the washings to the original water solution. The solution shall then be diluted to 250 cc. and an aliquot portion removed, neutralized with acetic acid, and titrated with copper sulfate solution. The end-point shall be determined by placing a drop of the solution on a filter paper next to a drop of potassium ferrocyanide solution. The completion of the titration is indicated by a reddish brown zone of copper ferrocyanide.

CALCULATIONS 
$$- \frac{\text{Cc. CuSO}_4 \text{ soln.} \times 3.75}{\text{Cc. taken for titration}} = \text{per cent CS}_2.$$

NOTE—The above quantity of alcoholic caustic potash is sufficient if the benzol contains less than 5 per cent of carbon bisulfide. If it contains more, a smaller sample should be taken. In this case, the formula for calculation must be modified accordingly.

#### TEST E8-PARAFFINS

APPARATUS—Babcock milk bottles. Centrifuge. Pipette, 10 cc. funnel, with capillary stem.

REAGENTS—Fuming sulfuric acid, 20 per cent free  $SO_{\delta}$ .

METHOD-IO cc. of the benzol to be tested shall be measured into the Babcock bottle, and 10 cc. of the fuming sulfuric acid slowly added to it, cooling the bottle in a bath of ice water during the addition of the acid, and shaking the bottle vigorously after each addition in order to thoroughly mix the contents. After the addition of the acid is complete, the bottle shall be removed from the ice bath, shaken until the temperature rises to about 40° C., and then alternately cooled and shaken for a period of 15 min., keeping the temperature below 40° C. Then the mixture shall be cooled again, 10 cc. more of the fuming sulfuric acid added, the whole mixed thoroughly and shaken and cooled as above, keeping the temperature below 40° C. Finally the mixture shall be allowed to stand for 30 min. at a temperature of about 35° C. Then the bottle shall be cooled in ice water and water added through the capillary stem of the funnel so that it enters below the surface of the acid. The water shall be added in small portions very cautiously and the bottle thoroughly shaken and cooled after the addition of each portion. When sufficient water has been added to bring the level of the liquid well up on the graduated portion of the neck, the bottle shall be placed in the centrifuge and whizzed for 5 min.

The paraffins present will rise to the surface and their volume shall then be read off in terms of the graduations on the neck of the bottle. This reading (in major divisions) multiplied by 2 gives directly the volume per cent of paraffins in the original material.

**PRECAUTIONS**—The graduated portion of the bottle should be 2 cc. divided into 10 major divisions. These are further subdivided into 5 or 10 divisions each. The readings should be taken in terms of the major divisions (0.2 cc. each).

NOTES—On diluting the sulfonation mixture with water it will frequently happen that a small quantity of solid sulfone will be formed, which, on centrifuging, will form a layer between the paraffins and the acid layer. This sulfone should not be mistaken for paraffins.

In benzol work we have found it necessary to carry on the dilution with water rather than concentrated sulfuric acid in order to prevent solution of paraffins in the mixture.

## TEST E9-HYDROGEN SULFIDE

APPARATUS—Balance. Separatory funnel, 250 cc. Beakers, funnels, desiccator, crucibles, etc.

REAGENTS—Sodium hydroxide C. P., 10 per cent solution. Bromine water, sulfur free, saturated solution. Barium chloride, 5 per cent solution.

METHOD—100 g. of the benzol shall be shaken thoroughly in a separatory funnel with 25 cc. of sodium hydroxide solution, the liquids allowed to settle and the lower layer drawn off into a beaker. The water layer shall be diluted to 400 cc., about 20 cc. of the bromine water added, the mixture acidulated with hydrochloric acid, the excess bromine boiled off and the sulfuric acid in the solution precipitated in the usual manner with barium chloride. The barium sulfate shall be filtered and weighed. A blank determination shall be made on the same amounts of the materials used in the analysis and the weight of barium sulfate deducted from that obtained from the benzol.

CALCULATIONS—Weight of barium sulfate  $\times$  0.1460 = per cent of H<sub>2</sub>S.

NOTES—Before proceeding with determinations of  $H_2S$  and  $SO_2$  a qualitative test should first be made in order to determine which of the two is present. This can best be done at the time of performing the distillation test, E4 or E5, by hanging strips of moistened lead acetate paper and starch iodate paper on the end of the condenser tube. If the lead acetate paper shows discoloration,  $H_2S$  is present, but not  $SO_2$ . In this case both papers will usually be discolored. If the lead acetate paper shows no discoloration but the starch iodate paper develops a blue color,  $SO_2$  is present but not  $H_2S$ . If neither paper shows discoloration, neither is present. As  $H_2S$  and  $SO_2$  mutually react both cannot be present simultaneously.

TEST EIO-SULFUR DIOXIDE

Apparatus, reagents, and method of analysis are precisely the same as Eq.

CALCULATIONS—Weight of barium sulfate  $\times$  0.2744 = per cent SO<sub>2</sub>.

TEST EII-SOLIDIFYING POINT OF PURE BENZOL

APPARATUS—Test-tube 5 in. long by 1 in. inside diameter. Thermometer, 0° to 80° (see D6).<sup>1</sup> Beaker, 400 cc. capacity.

<sup>1</sup> THIS JOURNAL, 10 (1918), 820.

METHOD—About 20 cc. of the benzol to be tested shall be poured into the test-tube and cooled in a bath of ice and water contained in a beaker, stirring continuously with a thermometer. When the solid benzol begins to separate the temperature will remain constant for some time. This temperature shall be taken as the solidifying point.

ACCURACY— $\pm$  0.05°.

#### LIGHT OIL

This material is tested for water, specific gravity, tar acids, and tar bases as described under heavy oil tests.<sup>1</sup> Other special tests are made as follows:

### TEST F5-BULB DISTILLATION

All matter as to apparatus, method, precautions and notes as given under E5 for materials boiling substantially above 135° C. apply to this test on these materials.

SPECIAL NOTE—With light oil, a dry point is ordinarily not taken, the distillation being continued only until about 95 per cent of the material has distilled over. Readings should be taken at first drop and every even 10° C.

## TESTS FÓ AND F7-TAR ACIDS (CONTRACTION AND LIB-ERATION METHODS)

These should be carried out exactly as given under HII and HI2.

#### TEST F8-HEMPEL DISTILLATION

APPARATUS—Flask, short ring neck, 200 cc. Hempel tube. Condenser and stand. Thermometer, 0° to 400° (specifications as under C9).<sup>2</sup>

The assembly of the apparatus is shown in Fig. XVII.

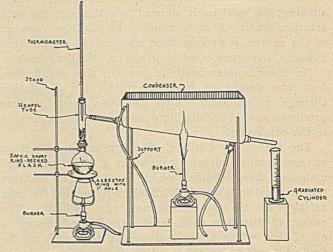


FIG. XVII-ASSEMBLY OF HEMPEL EVALUATION TEST FOR LIGHT OIL

METHOD—After the extraction of tar acids from 100 cc. of oil the residual oil shall be placed in the 200 cc. bulb and the apparatus assembled as in Fig. XVII. Heat shall be applied and the distillation conducted at the rate of 1 to 2 drops per sec. The volume which has distilled at 130° C., 170° C., and 200° C., shall be noted and recorded. The flame shall be removed when the thermometer reaches 200° C.

<sup>1</sup> THIS JOURNAL, **10** (1918) 911. <sup>2</sup> Ibid., **10** (1918), 819. NOTES—This test is a very rough evaluation test used for comparison purposes between oils. The  $130^{\circ}$ fraction roughly represents crude benzol and toluol; the  $130^{\circ}$  to  $170^{\circ}$  fraction, crude solvent; and the  $170^{\circ}$ to  $200^{\circ}$  fraction, heavy naphtha. If more exact information is desired, the test given under F10 should be used. The residue in the bulb should be preserved for Test F9 if this is desired.

## TEST F9-CRUDE NAPHTHALENE

## APPARATUS-Same as used under H17.1

METHOD—The residue above 200° C. obtained in Test F8 shall be transferred to the copper beaker, cooled to 15.5° C., and held at this temperature for 30 min. It shall then be filtered and pressed as described under H17. The weight of dry solids divided by the specific gravity of the original oil gives the per cent by weight of crude naphthalene.

TEST FIO-DETERMINATION OF BENZOL AND TOLUOL

APPARATUS—Distillation apparatus shown in Fig. XVI. Partial condenser distillation apparatus shown in Fig. XVIII. We shall be glad to furnish a detailed drawing of this apparatus to any who desire to procure the outfit. Three thermometers,  $0^{\circ}$  to  $200^{\circ}$ , previously standardized, and accurate to at least  $0.5^{\circ}$ . One thermometer,  $70^{\circ}$  to  $120^{\circ}$ , graduated in  $0.2^{\circ}$  intervals. One thermometer,  $110^{\circ}$  to  $160^{\circ}$ , graduated in  $0.2^{\circ}$  intervals. Three graduated cylinders, capacity 100 cc. One separatory funnel, capacity 2 liters. Westphal balance. Hempel distillation apparatus shown in Fig. XVII. Steam distillation apparatus.

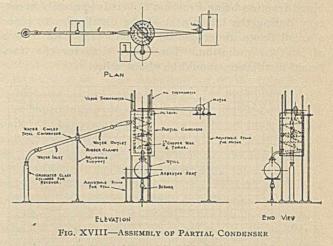
REAGENTS—Sulfuric acid, 60° Bé., commercial. Sulfuric acid, 66° Bé., commercial. Caustic soda solution, 10 per cent. Pure toluol, boiling within  $1^{1}/2^{\circ}$  C., sp. gr. at 15.5° C. not less than 0.870.

METHOD: Preparation of Sample—100 cc. of the sample to be analyzed shall be distilled following the procedure of E5. A larger sample of the oil, accurately measured at  $25^{\circ}$  C., shall now be distilled, using a Hempel column and collecting the fraction boiling below 160° C. The difference between this fraction and the original sample shall be noted as "heavy oil." The size of sample taken shall be so regulated by the results obtained in the preliminary boiling test that about 1000 cc. are obtained in this distillation. If the preliminary distillation shows 90 per cent or more at 160° C., the Hempel distillation may be omitted.

Acid Wash—The fraction up to  $160^{\circ}$  C. shall now be washed in a separatory funnel with 1 per cent by volume of  $60^{\circ}$  Bé. sulfuric acid, care being taken that the oil is kept cool during the washing. The acid sludge shall be drawn off and the oil washed with three successive portions of 2 volumes each of  $66^{\circ}$  Bé. sulfuric acid, the acid sludge being drawn off after each washing. The oil shall finally be washed with a dilute solution of caustic soda and this drained off. The washed oil shall be put into a steam distillation apparatus and distilled with steam until no further oil comes over. The upper oil layer shall be carefully separated from the water in a separatory funnel and

<sup>1</sup> THIS JOURNAL, 10 (1918), 916.

measured at 25° C. The difference between this volume and the volume before washing is noted as "loss in washing" and represents unsaturated hydrocarbons. The refined fractions so obtained should consist entirely of benzol, toluol, solvent, and possibly saturated paraffin hydrocarbons.

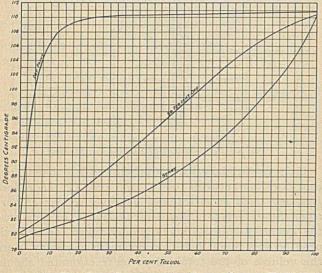


If the preliminary distillation showed less than 40 per cent distilling between 100° C. and 120° C., this refined fraction should be mixed with an equal volume of pure toluol before being subjected to analysis. In this case the quantity of material originally taken for analysis need be only about half that normally necessary, since the volume of the total oil to be fractionated should be 700 to 1000 cc.

Fractionation of Material-The refined fraction, which should approximate one liter, shall now be introduced into the 11/2 liter bulb of the partial condenser apparatus. The tank of the partial condenser shall be filled with a high boiling oil agitated by means of a small motor-driven agitator. The oil in the tank shall be heated up to 70° C. and the distillation of refined oil begun. The material in the flask shall be kept boiling vigorously so that the flame under the partial condenser may be turned off and the temperature continue to rise from condensation of vapors. The distillate shall be collected in 100 cc. cylinders, these being changed when nearly full, brought to a temperature of 25° C., and measured. As the temperature of the oil approaches 80° C. the distillation will very nearly stop and when very near the temperature of 80° C. a sudden increase in the rate of distillation will be noticed. This is when the benzol begins to come over in large quantities. The receiver shall now be changed and all fractions up to this point combined. This shall be called Fraction A.

The distillation shall be continued, allowing the temperature of the oil in the oil bath to gradually rise. The rate of distillation will gradually slacken until just below 110° C., when it is again practically stopped. At about this temperature the rate will again suddenly increase, the toluol coming over. When about 50 cc. of material have distilled beyond this point, the receiver shall be again changed and the fractions between the benzol cut and the toluol cut combined into Fraction B.

As the temperature of the oil bath continues to rise the rate of distillation will again decrease and will suddenly increase when the xylol boiling range is reached at about  $137^{\circ}$  C. The third cut shall be made when about 50 cc. of this material have distilled over. The distillation shall be stopped at this point, this combined fraction being Fraction C. It is generally necessary during the latter part of the distillation to place a small flame under the oil bath to take care of loss of heat by radiation. The entire time for the fractional distillation should be about 2 hrs.



CURVE 1-TEST F10. DISTILLATION OF BENZOL-TOLUOL MIXTURES

Interpretation of Results—100 cc. portions of Fractions B and C shall be submitted to distillation following the procedure of E4, temperatures being observed at start, 50 per cent off, and dry. The distillation of Fraction B shall be made using a 70° C. to 120° C. thermometer, and the distillation of Fraction C using a 110° C. to 160° C. thermometer. All temperatures shall be corrected for barometric reading, the correction factors for one millimeter of difference being as follows:

Fraction B-0.045° C.; Fraction C-0.050° C.

Fraction A should contain no toluol and shall be regarded as benzol.

Fraction B is a mixture of pure benzol and toluol with a very small amount of xylol. Its composition shall be estimated by reading on Curve 1, giving the boiling tests of benzol-toluol mixtures, the percentage of toluol corresponding to the temperature at which 50 per cent of the material was distilled off. The dry point of the distillation shall then be compared with the dry point curve of Curve 2 and the per cent xylol estimated. This percentage shall be deducted from the toluol. (This fraction should not contain more than 2 per cent of xylol.) From the percentage composition of the fraction so obtained and from its volume the actual amount of benzol, toluol, and xylol in it are figured.

Fraction C shall be similarly distilled and the percentage of toluol in it obtained from Curve 2 by the temperature at which 50 per cent was distilled off. This fraction should contain nothing but toluol and xylol. The actual amount of toluol is calculated from this figure and the volume of the fraction. From these figures the total volume of benzol and toluol in the original oil are determined. The toluol figure so obtained must of course be corrected for any pure toluol added before the fractionation.

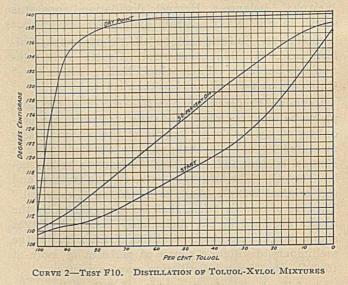
Correction for Parafin Hydrocarbons—If paraffin hydrocarbons are present in the original oil they will of course appear along with the benzol and toluol and their presence here can be corrected for. This correction is made by determining the gravities of the three fractions, B, C and D, accurately at 15.5° C. by means of the Mohr-Westphal balance following the procedure of H4.<sup>1</sup> Assuming a specific gravity of 0.884 for pure benzol, 0.871 for pure toluol, and 0.869 for pure xylol, the theoretical gravity of the three fractions can be calculated as follows:

$$0.884 \times \text{per cent benzol} + 0.871 \times \text{per cent toluol} = 100$$

<sup>100</sup> theoretical gravity of fraction The specific gravity of the aliphatic hydrocarbons corresponding to the three fractions would be, respectively, 0.720, 0.730, and 0.740. The percentage paraffin in the fraction can now be calculated as follows:

Theoretical sp. gr. of the fraction	-	a
Actual sp. gr. of fraction	=	b
Sp. gr. of corresponding aliphatic hydrocarbons	=	C
Per cent aliphatic hydrocarbons in fraction		$a - b \times 10$

The per cent paraffin so obtained must of course be corrected for in the benzol and toluol figures.



PRECAUTIONS—Care should be taken throughout all the operations that proper precautions are taken to prevent loss both in distillation and in handling. Corks should be tight and the distillate kept cool and covered as much as possible. For making cork connections, shellac is recommended.

REPORTING RESULTS—All results obtained are figured back to the original oil as follows:

Volume of constituent $\times$ 100	= per cent constituent
Original volume of oil	- per cent constituent
THE BARRETT COMPANY	
BATTERY PLACE, NEW YORK CIT	Y

<sup>1</sup> THIS JOURNAL, 10 (1918), 911.

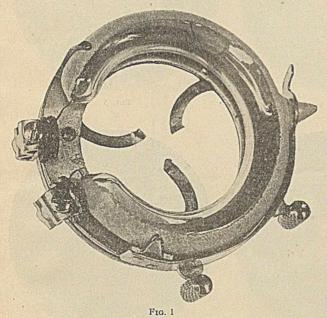
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## A NEW ILLUMINATOR FOR MICROSCOPES<sup>1</sup>

## SECOND PAPER By Alexander Silverman Received September 25, 1918

Since the publication of the first paper<sup>2</sup> about one year ago, a number of important improvements have been made in the illuminator<sup>3</sup> for microscopes therein described.



In the first paper the lamp holder was attached to the tube of the microscope by a clamp. In the newer form (Fig. 1) three fingers fasten the holder directly to the objective (Fig. 2). The fingers are iris-like in operation and are controlled by springs, so that it is possible to attach the illuminator to any objective.

The lamp described in the earlier paper was a 6 volt, o.7 ampere unit operated by dry or storage cells. The new lamp is a 9 volt, o.7 ampere unit of blue (daylight) glass and gives about 50 per cent more light. A rheostat has been devised which screws into an ordinary lighting socket. The rheostat has three taps, 107 volt, 112 volt, and 118 volt. A rheostat for 220 volt circuits is in preparation. If a greater light intensity is desired one can connect with a lower voltage tap. This is of advantage in photography. The normal voltage connection suffices for visual work.

Recent experiments with a colorless, one ampere, 13 volt lamp show that it can be employed safely. The lamp was placed in the holder, clamped to various objectives, and allowed to run continuously for half an hour, a period of time far exceeding any employed in actual operation. The objectives were not affected although the lamp carried an overvoltage of 15 per cent. Further, a colorless 0.7 ampere, 20 volt lamp was silvered instead of enameled. The silvered reflector reduces the amount of heat radiated towards the objective. Blackening the outer surface of the reflec-

<sup>1</sup> Presented at the Cleveland Meeting of the American Chemical Society, September 11, 1918. <sup>2</sup> THIS JOURNAL, 9 (1917), 971.

<sup>3</sup> U. S. Pat. 1,267,287. Can. Pat. 185,283. Other U. S. and foreign patents pending.

tor also reduces the heat traveling towards the objective. Both lamps yielded a light of much greater intensity than any hitherto employed. Results obtained will be discussed later.

The lamp reflector is placed at an angle of 45° to the plane surface of the stage. Low power objectives may be an inch or more above the stage, so a tube has been designed which may be clamped to the stage. The lower end of the tube will support the lamp at a constant distance from the object under examination and the objective may be raised or lowered inside the tube. The inner surface of the tube is dull black.

A shutter may at times prove desirable to cut the light off from one-half of the circular source. The experimental shutter employed for this purpose is a dull black disk which covers half of the lamp and is attached by prongs which are held by the lamp. Details are sometimes visible by this method which are obscured when the entire lamp is bare.

The illuminator may be attached to a microscope together with a vertical illuminator, thus affording a comparison of the separate effects of oblique and vertical light on an object. There is a marked difference in the appearance of metallurgical specimens under the two illuminators, the new one facilitating the study of depressions and showing details not hitherto revealed. In blow-holes and pits the slag content, etc., may be seen. The pits appear black by vertical light.

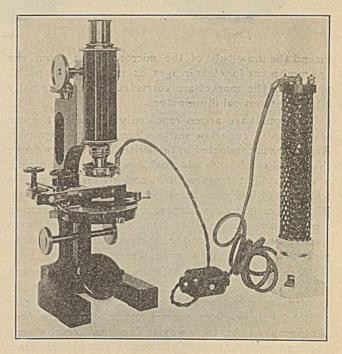


FIG. 2

When paper, textiles, insulating materials, biological specimens, etc., with light-absorbing surfaces, are examined by vertical light, little or none of the structure is visible. Under the new lamp a wealth of detail is seen which astonishes the observer who employs the device for the first time.

Should one wish to employ the new illuminator alone, and remove the vertical illuminator, it is necessary to . THE JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY Vol. 10, No. 12

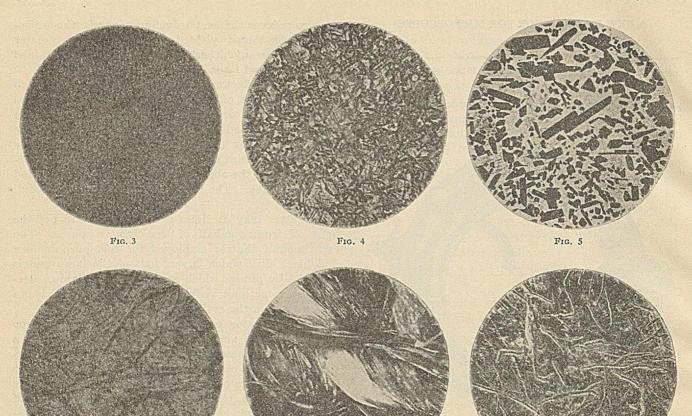


FIG. 6

FIG. 7

FIG. 8

extend the draw-tube of the microscope to about the 176 mm. point for clear images, as most microscopes at present on the market are corrected for the normally interposed vertical illuminator.

Questions have arisen repeatedly regarding the use of a lamp of such low wattage for photomicrography. Experiments conducted in the writer's laboratory prove that good results are obtainable with the 0.7 ampere, 9 volt daylight lamp with 8 and 16 mm. objectives and those of lower power, when the eyepiece is removed. With the colorless 0.7 ampere, 20 volt silvered lamp or the one ampere, 13 volt lamp it is unnecessary to remove the eyepiece, as the light intensity is ample to yield clear images on the ground glass.

Focusing may be facilitated by greasing the ground glass with a little vaseline, subsequently rubbing it as dry as possible with a cloth. Bronzes, highly polished ball bearings, enamel, paper, etc., have been photographed in this way. The best results were obtained with Hammer Ortho extra fast and Hammer Ortho nonhalation plates.

Figs. 3, 4, 5, 6, 7 and 8 show results obtained with the 0.7 ampere, 20 volt silvered lamp with exposures of from 15 to 30 seconds, using a 16 mm. objective and 10X eyepiece. Fig. 3 is a blue enameled steel; 4, a steel casting, 0.37 carbon, not pressed or heat treated; 5, an iron-zinc alloy obtained in zinc manufacture; 6, a piece of blue cover paper; 7, a piece of cloth; 8, a cast iron specimen. In conclusion, the writer wishes to express his appreciation to the scientists in various fields who have experimented with the new device and made suggestions which have resulted in valuable improvements in methods of application.

School of Chemistry University of Pittsburgh Pittsburgh, Pa.

## A SPECIAL STOPCOCK FOR DROPPING LIQUIDS AR-RANGED FOR EQUALIZING THE PRESSURE ABOVE AND BELOW THE OUTLET IN THE STOPCOCK<sup>1</sup>

By HARRY L. FISHER Received June 4, 1918

The stopcock described herein was designed in connection with a generator for carbon dioxide which was to be used alternately with pressures below and above atmospheric in the final preparation of cupric oxide and for the determination of nitrogen by the Dumas method according to the modification of Fieldner and Taylor.<sup>2</sup>

Ordinarily an outside tube connecting the top of the reservoir of acid with the upper part of the container of the carbonate is used. In this new apparatus the connection is made by means of an annular groove in the key of the stopcock so that no matter which position the key occupies there is always communica-

<sup>1</sup> Presented at the Boston Meeting of the American Chemical Society, September 10-13, 1917.

<sup>2</sup> Fieldner and Taylor, THIS JOURNAL, 7 (1915), 106.

tion between the atmosphere in the lower flask and the atmosphere in the upper flask. One arm of the stopcock is extended until it opens above the liquid in the upper container. The liquid enters at an aperture in the lower part of this extended arm and is delivered through a small glass tube sealed in at this opening. The entire arrangement is more clearly understood by a glance at the accompanying diagram. Two different styles were made, using the same principle in each.

 $\Box$ 01 10mm 60 Fig.1a 20 20 Fig.1 FIG. 1 -LONGITUDINAL SECTION FIG. 1a-CROSS SECTION AT CENTER FIG. 2 -LONGITUDINAL SECTION ADDITIONAL DIMENSIONS Fig. 1 Mm. Fig. 2 Mm. Length of stopcock barrel ... 35 35 Outside diameter of inner tube...... Inside diameter of outer tube...... 53 10 13 9.5 Inside diameter of outer tube...

If the flasks are used as shown they must be securely fastened by clamps close to the lips. The upper flask can be filled through a funnel attached by means of a piece of rubber tubing. The liquid will flow down the inside walls and not drop into the extended tube. The arrangement and kind of flasks can be changed as desired, and it is believed that the apparatus will be of service elsewhere. I wish to acknowledge my thanks to Mr. W. Wiegand of the firm of Eimer and Amend, New York City, for his interest and skill in making these two stopcocks. LABORATORY OF ORGANIC CHEMISTRY

COLUMBIA UNIVERSITY, NEW YORK CITY

### A NEW TIMING DEVICE FOR SIMPLIFYING THE THER-MOMETRIC READING OF CALORIMETRIC DETERMINATIONS

By CHAS. A. MYERS, JR. Received May 18, 1918

At the beginning of the war the chemical laboratory of the New York Navy Yard was called upon to do all the chemical analyses of coal used by the fleet and its auxiliaries in the northern district. This wrought a tremendous increase in the work which the laboratory in normal times was expected to do; but notwithstanding the increase in the number of analyses it was essential that there should not be any sacrifice in the accuracy to which these operations were ordinarily accustomed. The writer, who has for some time been engaged in the work in question, has developed an electrical timing device for calorimeters which he believes would be of great assistance to anyone called upon to determine calorific values under such circumstances, where radiation factors are involved.

One of the chief advantages of this timing device is its absolute accuracy in giving the operator the exact second at which to read the thermometer. The instrument, moreover, relieves to an almost unbelievable

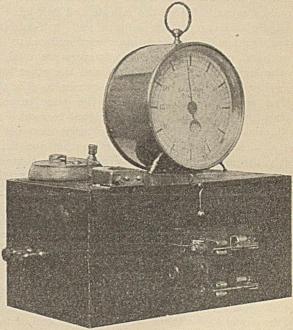


FIG. I

extent the strain on the operator who may be called upon to make constant readings over an extended period of time. With this device it is no longer necessary to divide attention between the stop watch and the thermometer, first looking at one and then the other, as an audible warning signal is given 5 seconds before the time to read, and a second signal at the moment at which the reading should be taken.

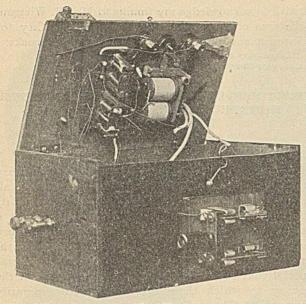
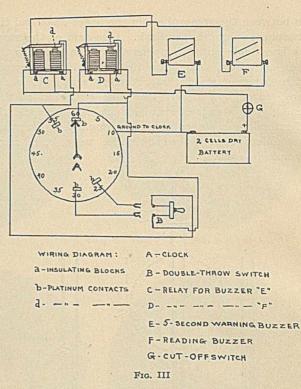


FIG. II

A further advantage is that almost any number of calorimeters may be operated at one time by this device, it being simply necessary to have the signals loud enough to be heard by all of the operators.

The device consists of a clock put out by one of the large photographic supply houses which has a large second hand making one complete revolution every minute. On the face of this clock are cemented four platinum-foil squares arranged so that contact will be made 5 seconds before the minute and half-minute, and again exactly on the minute and half-minute. Contact is made by a fine platinum wire soldered to the second hand of the clock. Two buzzers are used to give the signals, one of high pitch and the other low. The writer selected the high-pitch buzzer to give the warning signal 5 seconds before the time to read and the low-pitch buzzer for the signal to read. As the buzzers consume a relatively large amount of current it is impossible to make contact for them directly through the platinum wire and the contacts really operate two relays and these in turn pass the



current through the buzzers. The relays are made from common nails about  $1^{1/2}$  in. long turned down in a lathe and wound with eight layers of No. 36 double silk covered copper wire. A small piece of platinum is soldered to the end of one of the magnets of each relay ( the one furthest from the hinge) and this makes contact with another piece of platinum soldered to the armature, thus closing the circuit to the proper buzzer. The relay magnets and their supports are mounted on a hard rubber base which insulates the armature from the magnets when current is not flowing through the latter. A double switch is provided to cut out the half-minute readings when these are not desired and a single point switch to shut off all readings. The details of the wiring are shown clearly in Fig. III.

CHEMICAL LABORATORY NAVY YARD BROOKLYN, N. Y.

## ADDRESSES

## SOME APPLICATIONS OF PHYSICAL CHEMISTRY IN THE COAL-TAR INDUSTRY

## By WILBERT J. HUFF

This paper will be divided into two distinct parts, the first of which deals with volume relations in solidifying creosotes, while the second applies to the vapor densities of coal-tar fractions.

I-VOLUME RELATIONS OF SOLIDIFYING CREOSOTES

Since liquid coal-tar products are regularly sold by volume, the exact determination of the variation of volume with temperature is of great economic importance to both distiller and consumer. The standard temperature for oil measurements is usually 60° F., although in the case of creosote oil roo° F. has been somewhat generally adopted. Since it is obviously

<sup>1</sup> Read before the New York Section of the Society of Chemical Industry, May 24, 1918. impossible to bring tank car quantities to the standard temperature before gauging their volume, the shipper determines the volume at the shipping temperature and calculates the volume at 60° F. by means of a coefficient of cubical expansion; the receiver invoices at the temperature at which he happens to get the car and calculates by means of the same coefficient to the same temperature.

Now the trade has found it difficult to obtain concordant results between measurements taken at shipping and receiving points on creosote oil in tank cars and tank vessels. The discrepancies have in some instances amounted to as much as 5 per cent of the volume of oil handled.

Adjustments, however, were necessary not only in companyconsumer shipments, but also in inter-plant shipments, and even in inventory calculations at the same plant. Clearly, something was wrong.

Some earlier work on volume relations in creosote oil was car-

ried on by Mr. H. E. Lloyd, of The Barrett Co., and the results obtained by him, although not conclusive, fully indicated the need for a more searching investigation into the problem.

One of the first things that attracted my attention while considering this problem was the mental haze of the practical employee when dealing with the simple mathematical relations involved in calculating coefficients of cubical expansion. I have found by personal observation and experience that very many chemists (strange to relate) do not relish the mental gyrations of the mathematician. Even engineers had been somewhat lax, for the trade had been making no correction for the coefficient of cubical expansion of the container and in consequence did not calibrate the container at any definite temperature.

Although it is a repeating of very elementary matter, I will give here the formulas which are used in determining and applying coefficients of cubical expansion.

The change in volume per unit volume per degree change in temperature is called the coefficient of cubical expansion.

Thus:

$$V_2 = V_1(1 + at)$$

in which a is the coefficient of cubical expansion.

Since in practice the container is always an expanding material, the apparent expansion is less than the real. The container expands, partly compensating for the expansion of the material.

The relations are generally expressed by the equation

$$A + C = T$$

in which A is the apparent coefficient of cubical expansion of the liquid, C is the coefficient of cubical expansion of the container, while T is the true coefficient of cubical expansion of the liquid.

This relation is strictly true only for the case where the container is always kept full, as in most specific gravity determinations with a pycnometer. When the liquid rises and falls in a steel container the deviation in the apparent coefficient from this relation can be shown mathematically to be about 3 parts in 100,000 per degree Centigrade.

This is of course much smaller than the errors of measurement in practice. Consequently the form given above (which is exceedingly simple) may be regarded as correct for all cases.

One of the first points considered was the relative effects of the variations in conditions in a large container, as for instance: stratification, sedimentation, inequalities of temperature, etc., which would not be pronounced in the small volume of a specific gravity bottle in which the previously used coefficient of cubical expansion of creosote oil had been determined. Accordingly, a hollow iron container with a capacity of about  $2^{1}/_{2}$  gal. was fitted with a screw cap carrying a glass tube to serve as the neck of a pycnometer, and with three thermometers placed at different distances from the center. This was placed in a 50gal. water bath provided with an agitator, and suitable burners, etc., for applying heat. A glass pycnometer was placed in the same bath in order to duplicate the work in a small volume. No essential difference in results was obtained, showing that the difficulty lay somewhere else.

The iron container was twice calibrated with water and the apparent coefficients of expansion of water in iron calculated over the ranges: 15.5–25° C., 25–38° C., 38–60 C., 60–80° C.

These observed values were then subtracted from the true zero ones, giving by difference the coefficient of cubical expansion of iron. The mean of one set of experiments gave 0.000037for this, while the mean of another set gave 0.000036. These results were considered very satisfactory, for the accuracy of 0.00001 to 0.00002 is from 5 to 10 times more than the previously accepted coefficient of cubical expansion of creosote oil (0.00079 per degree C.). The subsequent work with oils, however, was probably not quite so accurate, for the oils were much harder to bring to a constant volume, probably because of a lower heat conductivity.

In the work with oils the container was filled at  $80^{\circ}$  C. and later made to the mark at about  $60^{\circ}$ ,  $38^{\circ}$ ,  $25^{\circ}$ ,  $15.5^{\circ}$ , with weighed water. The pycnometer was made to mark with the oil when used with liquid oils. With solid oils it was filled at  $80^{\circ}$ , made to mark with oil at  $60^{\circ}$ , and then with water at temperatures below  $60^{\circ}$ .

Two creosote oils were examined: A refined liquid creosote oil, hereafter referred to as No. 1, which does not solidify in the range covered, and an oil representing a commercial grade of creosote oil according to the standard specifications of the American Railway Engineering Association, hereafter designated as No. 2, which gave a small amount of crystals at  $15.5^{\circ}$ C. The coefficients found for these oils checked very satisfactorily in duplicate experiments both in the large container and the small specific gravity bottle. The mean true coefficients found (0.000703 for No. 1 and 0.000724 for No. 2) were slightly lower than the previously accepted value (0.00079). The apparent coefficients in steel tank cars would be even lower. These findings, however, did not explain the discrepancies encountered in practice.

The thing which was especially interesting to me was the absence of variation in the coefficients with temperatures. The coefficient of cubical expansion of water shows a huge variation over the interval in question  $(15^{\circ}-80^{\circ} \text{ C}.)$ . This variation amounts to from 200 to 300 per cent.

The influence of salts upon the coefficients of cubical expansion of these oils was next studied by salting the same oils with pure naphthalene for a limpid point of about  $40^{\circ}$  C.

This mixture consisted of No. 1 oil 71.5 per cent and naphthalene 28.5 per cent by weight. A little more than 30 per cent distilled below 235° C. In the upper ranges this mixture contracted regularly with descending temperature and gave the coefficients found for the original No. 1 oil. At temperatures below 38° C., however, the crystallization caused an enormous shrinkage. In one experiment the average coefficient between 38° and 25° was from 4 to 5 times as great as that for liquid creosotes. In a duplicate experiment the value was from 3 to 4 times as great. This abnormal behavior was always exhibited below 38°, that is, below the temperature at which crystallization became important. The expansion and contraction observed was of course the resultant of three factors: (1) The mechanical expansion or contraction of the liquid phase. (2) The mechanical expansion or contraction of the solid phase. (3) The volume change due to the solution or crystallization of the solid phase. Now it is very probable that the coefficient of cubical expansion of solid naphthalene is much less than that of the liquid creosotes. (Beilstein reports the density at 4° and 15° C. to have practically the same value.) Undoubtedly these huge and irregular coefficients are caused by the crystallization.

Naphthalene dissolves in creosote oil with an increase in volume; I qt. of naphthalene and 3 qts. of a salt-free creosote oil will make more than I gal. of mixture.

The magnitude of the volume change accompanying the solution or crystallization is unfortunately very large. Some of the experimental results obtained showed that an error of as much as 404 gals. per 10,000 gals. in a temperature interval from 110° to 70° C. might easily be possible, using the old coefficient of cubical expansion.

The word "unfortunately" is used advisedly. The process of crystallization and solution is very slow when contrasted with the mechanical expansion or contraction of the solid and liquid phases. In consequence, with varying temperatures there may be, and probably often will be, incomplete equilibrium between the two phases. Accordingly, the observed volume of the total will vary a great deal with the immediate past history of the mixture. It is only to be expected, therefore, that the results obtained in measuring the coefficient of expansion of a partially solid oil will not check unless great care and a sufficiently long time is allowed to elapse at each temperature to insure that the crystallization or solution has attained equilibrium. Since in actual practice it is very often not desirable or even possible to maintain a tank or tank car at exactly the same temperature for a sufficiently long time to insure equilibrium between the solid and liquid phases before determining the volume, the practical value of such a coefficient, even when obtained with the greatest care, is very doubtful. Variations in the amount of crystallizable substances from time to time in the same grade of oil will seriously affect the coefficient.

Another possible complication is the variation in the character of the crystallizing solid. Suppose anthracene crystals appeared instead of naphthalene crystals, what would happen then?

This point was investigated by dissolving crude anthracene in the No. 1 oil. The work was abandoned, however, because of the extremely slight solubility of this compound in this oil; less than 5 per cent of the solid gave a limpid point of  $40^{\circ}$  C., while it took more than 28 per cent of naphthalene to give the same limpid point. With less than 5 per cent of anthracene present, it was not deemed worth while to examine the volume relations of the mixture.

Naphthalene is, of course, the most important solid. Moreover, its similarity in physical properties, composition, and structure to other coal-tar compounds leads one to believe that an analogous effect occurs when most of the other solids crystallize or dissolve.

The magnitude of the error, and the inherent insurmountable obstacles encountered when one attempts to predict the volume of an oil at a temperature at which it may be partly solid, may ultimately revolutionize the present practice of buying and selling oils by volume.

The simplest expedient, of course, is to buy and sell by weight. At present, however, such a departure is so radical that it is practically impossible.

It is probable that a temperature of 100° F. will be widely adopted as the standard, displacing the 60° F. of the present, since at 100° F. the creosotes are liquid. The trade situation was somewhat amusing—we had been buying and selling gallons at 60° F. without knowing the volume relations which relate 60° F. to the customary temperatures of trade.

#### II-THE VAPOR DENSITIES OF COAL-TAR FRACTIONS

Although the composition of the higher fractions from the distillation of coal tar has long been a subject for study and speculation, and many of the compounds present have been isolated and identified, the quantitative composition of these interesting mixtures still remains a matter of mystery. It is probable, however, that the number of compounds present is very great.

This question was of especial concern to the engineering department of The Barrett Company in the design of large capacity condensing systems, since a knowledge of the exact composition would give by a simple calculation the vapor density of any fraction, and in turn a key to a design for a condenser embodying economical construction and efficient fractionation.

It fell to the lot of Mr. Gainey and myself to investigate these vapor densities which, of course, could be ascertained only by experiment.

Of all the methods for determining vapor densities, the Victor Meyer is the best suited for a problem of this kind, since it is applicable over a very wide range of temperatures and pressures and is equally useful for pure compounds and mixtures. Other methods afford some of these advantages but not all. Thus the Dumas could be used at the temperatures and pressures desired but, unfortunately, is inapplicable

to mixtures whose components have different boiling points. The Dumas, you will remember, calls for a light glass bulb drawn to a point and weighed. The substance under examination is introduced and the bulb is then placed in a constant temperature bath while a certain pressure is applied (generally atmospheric) until the bulb is completely filled with vapor and the excess vapor has been removed. The bulb is then sealed off and weighed. In this procedure, the lower boiling components would probably be removed from the bulb before the higher were completely vaporized, so we could not employ this to determine the vapor densities of fractions of the coaltar distillate. The Gay-Lussac-Hofmann method, which consists in the introduction of the substance into the vacuum above an upright barometer, can be employed equally well for pure compounds or mixtures, but is unfortunately limited to temperatures where mercury exerts no appreciable vapor tension, that is, below 150° or 175° C., and could not be used for coal-tar fractions whose boiling points in some cases are higher than 400° C.

For the sake of a clear understanding of what follows, I will recall the principles which are involved in the Victor Meyer method of determining vapor densities by air displacement.

In its simplest form the apparatus for this method consists of a long "pear-shaped" glass tube provided with two side tubes near the upper end. One of these side tubes is connected through a rubber tube to a gas burette. The lower portion of the glass pear is brought to a temperature which is sufficiently high to insure complete volatilization of the test material. This material is then introduced through the stoppered opening in the top of the tube and dropped at the proper moment by withdrawing a glass rod thrust through one of the side tubes. Upon reaching the hot portion of the pear, the material vaporizes, driving up ahead of it and over into the gas burette, air, which, of course, does not condense and can be measured as soon as the system reaches equilibrium. From a knowledge of the weight of the material, the volume of the air driven over into the gas burette, and its temperature and pressure, it is possible to calculate the density of the test material in the vapor form.

A modification of the method consists in attaching the pear to a manometer and measuring the increase in pressure at constant volume caused by the volatilization of the test material. This modification is particularly useful when it is necessary to employ a diminished pressure to insure complete volatilization, since it is very difficult to measure an increase in volume in a system maintained at a very low pressure.

Such considerations are so preliminary and general that I feel compelled to apologize for presenting them to you.

The first consideration peculiar to the vaporization of these coal-tar distillates was the question of coking. To throw suddenly these hydrocarbon-containing mixtures upon glass surfaces heated to several hundred degrees Centigrade without cracking and coking them was indeed a problem, especially when the boiling point ranges ran above  $350^{\circ}$  and  $400^{\circ}$  C. Decomposition by cracking and coking had to be guarded against in the distillation which gave the test fractions also.

A composite oil typical of the distillate from coal tar, between first runnings and hard pitch, was distilled in the laboratory and cut to 50° C. fractions. This oil began boiling at 200° C. under atmospheric pressure, and the distillation was continued under atmospheric pressure for two fractions until the vapor temperatures reached 300° C. In order to forestall cracking, the distilling bulb was then allowed to cool and an absolute pressure of 50 mm. of mercury was then applied. The oil began to distill once more at 175° C. and continued to distill until a temperature of  $370^{\circ}$  C. was attained. Further heating only produced decomposition into non-condensing vapors. In all, 87 per cent of the oil distilled and five 50° fractions were obtained.

and the second second as second as we will		VAPO	DR DE	INSITY RESULT	rs .	
Сомроинд	Formula	B. P. at 760 mm.		at 0° Č. a	density nd 760 mm. oer cc. Obtained	COAL-TAR FRACTIONS Boiling Point Ranges
Naphthalene di-hydride Naphthalene Methyl naphthalenes Diphenyl Acenaphthane	C10H s C11H10 C12H10	200–210° C. 218° C. 240–243° C. 254° C. 278° C.	194 124 124	0.00579 0.00572 0.00634 0.00688 0.00688	0.00579	199–249° C. under 755 mm. Hg 249–296° C. under 755 mm. Hg
Anthracene Methyl anthracene. Chrysene	C14H10 C15H12 C16H10	360° C. Above 360° C. 436° C.		0.00794 0.00858 0.00902	0.00691 0.00867 0.1047	180–229° C. under 50 mm. Hg 229–276° C. under 50 mm. Hg 276–322° C. under 50 mm. Hg

A number of preliminary experiments were made to fix a method of procedure. It was found advisable to confine the test fractions in Woods metal bottles which melted immediately and threw the entire contents in contact with the hot glass surface. Glass containers were unsatisfactory; the lower boiling material passed into the vapor form, reached the cool portion of the tube and condensed, before the higher boiling material was completely volatilized. Considerable time was spent investigating the possible coking of the fractions in the Victor Meyer pear. The criterion for coking was the appearance of the glass pear, which became badly discolored with carbon when the pear was heated much above 360° C. In a mercury vapor bath (giving a temperature of 357° C.), however, no coking occurred. This was extremely fortunate, for it permitted the use of this vapor bath as the heating agency, giving a temperature which remained constant without attention and was easily reproduced.

The discovery that coking became serious above some 360° or 370° C., coupled with the fact that two of the fractions had boiling point ranges higher than this when under atmospheric pressure, rendered it imperative that an apparatus capable of measuring vapor densities under diminished pressure be fitted up.

Accordingly a flexible mercury manometer made from two glass tubes, a rubber hose, and an upright meter stick was attached to the Victor Meyer tube and the tube evacuated to a low pressure by means of a vacuum pump, the fraction volatilized and the change in pressure noted. The calculations for this low pressure work involved a factor known as the tube constant. This constant depended upon the size of the tube; thus, when a tube of a certain size is used half as much pressure is developed by a given amount of vapor as is developed when a tube of only half that certain size is used, *i. e.*, in a tube twice as large, only half the pressure is developed.

The constant was determined by volatilizing in the tube at the temperature of the experiment a known amount of a compound possessing a known vapor density. The determination of this constant proved quite a bugbear to Mr. Gainey and myself. The slow deliveries on special glassware due to war conditions compelled us to blow our fragile tubes at the blast lamp. We would often carefully standardize a tube in duplicate (consuming several days in the operations) only to break it by some accident before we could use it for a determination. You can then imagine us sweating over the blast lamp in the heat of last August while we blew another tube, hoping for better luck the next time.

In the above table are given our vapor density results, compared with the calculated vapor densities of a few well-known hydrocarbons whose boiling points place them in the range of the appropriate fraction.

The vapor densities of the first two fractions were obtained by determining the volumes of air driven into a gas burette in the standard Victor Meyer method, the third was obtained by packing the tubes with hydrogen whose rapid rate of diffusion into the volatilizing oil insured complete vaporization, the last two were obtained by the use of the manometer and the low pressure system. Mercury vapor was used as the heating medium for all the experiments.

#### ACKNOWLEDGMENT

The experimental material presented in this paper was obtained while I was engaged in physical chemistry research for The Barrett Company and is the product not only of my own efforts but also of the efforts of Mr. John Gainey, who so ably assisted me in the latter part of the work and who is now still engaged in extending it. My debt, however, is not limited to Mr. Gainey. It is owed to the administrative officers of the Research Department of The Barrett Company, to whom I extend my thanks for direction and advice.

It is my belief that physical chemistry is afforded no richer field for research and development than the coal-tar industry, so economically important to the country in peace and so prominent in the scheme of modern warfare. My short connection with this industry has led me to believe that it is only in its infancy and that many of its latent possibilities will be realized by the aid of physical chemistry.

RESEARCH DEPARTMENT THE BARRETT COMPANY NEW YORK CITY

## A MANUFACTURER'S EXPERIENCE WITH GRADUATE CHEMICAL ENGINEERS<sup>1</sup>

By S. R. CHURCH

## Received July 15, 1918

The writer has often objected to the term "Chemical Engineer." It seems to place chemical engineering alongside of civil, mechanical, and electrical engineering as one of the natural divisions of the engineering profession. We would define chemistry as the science of the composition of materials, and engineering as the science of works. Chemistry is therefore the fundamental science, as without some knowledge of the composition of materials an engineer will fail.

For the purpose of this paper the writer will consider that a chemical engineer means a graduate in engineering who has had at least four years of college training at an institution recognizing the engineer's need for knowledge of the composition of materials.

During the past two years we have employed in our General Manufacturing Department 100 student engineers. These men were employed, not to occupy at first a definite position, but to undergo a course of study in the Company's business and to fit themselves for positions in the engineering, operating or experimental departments of manufacturing, after a period of at least 6 months' training. In this training period the men receive instruction in the form of lectures on various products and processes by heads of the manufacturing and technical staff and are given special assignments for personal study of a product, process, manufacturing unit, laboratory, or works experiment, etc.

It is our purpose to have at all times about 10 to 20 men in the training period, and at the end of about 6 months to assign a student to a definite position, or release him, or under certain conditions to continue his probationary period.

The men are in general selected with a view to their apparent fitness to become assistant superintendents or foremen, but in a

<sup>1</sup> Paper submitted for the Proceedings of the American Association for the Advancement of Science.

few cases men have been employed because of special ability in line of designing apparatus, etc. These men ranged from 21 to 40 years of age and from newly graduated students to men having 10 years' industrial experience. Among them are civil and mechanical engineers, but a majority are graduates from chemical engineering courses. In the number are graduates from most of the engineering colleges and universities east of the Mississippi.

While the results have of course been almost as varied as the number of men engaged, yet certain observations have been made which may reflect the influence of the institutional training received by these men. It seems especially true of the chemical engineers that they lack ability to correctly evaluate measurements. They seem to have been taught that a result must be accurate to a certain decimal fraction, and attempt to apply this without reasonable sense of proportion.

They are usually careful and fairly good in the technique of experimental work but lack ability to discern from an unsuccessful experiment the suggestive feature that should point the way to further experiments. They appear not to have been impressed with the importance of qualitative results. They often fail to discern the value of an indicative result in an experiment that has partly or wholly failed in its primary object and lack the imagination which enables the exceptional student to see his way through an accumulation of data that to another is only material for a progress report.

At this point we might note that ability to write a really good comprehensive report is not possessed to a satisfactory degree by the majority. In some cases this is so serious that men entirely capable of doing good work have utterly failed to make good. Instructors do not perhaps realize to what a large extent the graduate will, during his first 6 months or year in commercial life, be judged by his written reports.

Another common failing of many of our chemical engineers is poor training in the graphic presentation of experimental data. The superiority of a well-plained chart over a series of tables, both in facility of interpretation and suggestiveness, does not appear to be well grounded in them. Many lack a good sense of relative values, such as enables the exceptional man to consider a sample of material, the report of a day's run on a still or mixer, only for what it is worth; and to avoid the loss of time and effort that the average student would expend on carrying out elaborate analysis or calculations on a premise having obvious limitations. A greater familiarity on the student's part with the general principles common to works practice might seem to be reasonably expected. As for instance that the value of accuracy in laboratory analysis depends absolutely on the accuracy with which the sample represents a given lot of material, and that knowledge of the limitations of accurate measurements or sampling outside the laboratory may save much time in eliminating refinement of procedure and calculation.

The writer is of the opinion that a comprehensive course in Chemical Engineering should cover at least 5 years and preferably six. He realizes that for various reasons, not the least of these being the tremendously increased demand for chemical engineers, many colleges will not extend their courses to a 5 or 6 year basis. He urges that especially in the shorter courses every effort be made to give the student a sense of values, a better touch with the work, and to develop his imagination so that he will see in the problem assigned to him not the possibility of solving the value of X and writing Q. E. D., but of coming to his employer with a suggestion that by raising the temperature of this reaction we may obtain an increased yield of 5 per cent; or by putting a worm conveyor here we can eliminate the work of two men.

The writer is a firm believer in long and thorough schooling, in painstaking, and in accuracy; but the man who has not been taught at school to eliminate the unnecessary in his work and way of thinking will be slow to perceive the value of the short cut in manufacturing.

It is too much to expect that all of the defects herein noted, which are in some degree common imperfections in all of us, can be cured in a 4, 5, or 6 year college course. The writer felt that criticism rather than commendation would be more helpful and has purposely omitted reference to the many good qualities possessed by the men we have employed.

THE BARRETT COMPANY 17 BATTERY PLACE NEW YORK CITY

## CURRENT INDUSTRIAL NEWS

By A. McMILLAN, 24 Westend Park St., Glasgow, Scotland

## BURMESE MONAZITE SANDS

The Geological Survey of India reports that an analysis made of the monazite sands of Mergui and Tavoy in Tenasserim, Lower Burma, taken from 28 locations, shows but 0.18 per cent of thoria in the heavy concentrates, which is equivalent to 0.00216 lb. of thorium oxide per cubic yard of the ground sampled and adds that such minute fraction is, of course, of no practical utility.

#### INCANDESCENT LAMPS

A new edition of their "Incandescent Lamp Handbook, No. 1A" has been sent out by the British Thomson-Houston Co., London, and contains particulars and prices of lamps of both the vacuum and the half-watt types, for standard lighting service. In addition, there is a great deal of information about the terms and definitions used in the lamp trade and the photometric units and standards employed in illuminating engineering. The lumen, which has been adopted as the unit of light rating for electric lamps by the engineering societies and lamp manufacturers of the United States and Canada and by the leading British lamp makers, is explained at considerable length and examples are given showing how lighting calculations are simplified by its use.

#### ALUMINUM AND ITS ALLOYS

Dr. W. Rosenhain, lecturing recently in London on aluminum and its alloys, said that the possibilities of aluminum and its alloys depended primarily on the lightness of aluminum. Lightness of itself, however, was of little value. What was required was a combination of great strength and lightness. This had been attained to an astonishing degree in the modern aluminum alloys. There were many moving parts in light machinery, such as cycles and sewing machines, in which the extensive use of light alloys would appear to offer a great field for real advance. For air craft and other purposes, it has the importance of a "key" industry.

#### PEAT FUEL

A method of treating peat for fuel purposes proposed by Mr. S. C. Davidson, Belfast, consists in disintegrating it, mixing it with 15 per cent of pitch and submitting it to a pressure of at least two tons per square inch in a hydraulic press. In this way its bulk is reduced to about one-third and it comes out of the press in a solid block looking like polished hardwood which burns with a steady yellow flame. From his experiments, Mr. Davidson believes that the peat will require only a short period of air-drying before treatment by this process.

Dec., 1918 THE JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY

### OILS FROM COAL TAR

Prof. Carl Goldschmidt, of Essen, and R. Friedlaender, of Berlin, both members of the recently formed Kohlchemie Konsortium, have recently issued a pamphlet, says the *Oil and Color Trade Journal*, **54** (1918), 962, calling attention to the advantages and possibilities of their so-called coal Liquefaction Process, *i. e.*, the synthetic manufacture of benzolenes, lighting, engine, and lubricating oil from lignite, generator tar, crude oil, and crude oil derivatives. They mention the cracking and separating processes of Zern, Walther, and Graele, whereby the constituent parts of tar boiling at higher temperatures are transformed into benzolenes. They also deal largely with the somewhat related Bergin process whereby with the aid of heat and hydrogen, both benzolene and lighting oils are obtained of a quality equal to those obtained from natural sources.

The chief primary raw material, lignite-tar, can be obtained from the heating of generators, for instance, in lignite briquette factories in which some 20,000,000 tons of lignite are worked up, glass kilns, paper mills, and the like, in which some 12,000,-000 tons are used to fire boilers instead of being gasified. In this way alone, 1,500,000 tons of tar are obtained for distillation, etc., and the gasification of lignite alone would suffice to supply Germany with all her requirements in enriched oil products. Until such gasification plant has been established everywhere steps should be taken to secure a steady importation of raw oil and more especially of raw materials for the synthetic manufacture of benzolene and oil. Such a raw material is a by-product in Russian, Roumanian, and Galician distilleries, which use large quantities of it as an inferior kind of fuel.

#### SODA AND SULFITE PULP

The Paper Maker, quoting from a German contemporary, states that in the sulfite process certain residues of the wood substance survive and are found in the paper, whereas by the alkaline process the purification is far more complete. These residues of cell content which are particularly to be found in the cells of the medullary rays, may be made visible by staining, and serve for the differentiation of soda and sulfite pulps. The residues are found even in bleached sulfite pulps and exist as aggregates or chains of small spherical elements. Their staining capacities depend on the presence of resin. With an aqueous alcoholic solution of Soudan III, with a little glycerin added, they are stained red; with zinc chloride-iodine solution, sulfuryellow. In preparing the pulp for microscopic examination care must be taken to avoid dissolving the resin by the caustic soda. Medullary ray cells are so numerous that the presence of even 5 to 10 per cent of sulfite pulp in a mixture can thus be detected. For quantitative estimation of mixtures of sulfite and soda pulps a solution of rosaniline sulfate with a little alcohol and sulfuric acid is of service. The contents of the pitted pores are strongly stained in the case of the sulfite pulps, but not with soda pulps. The inner side of the fiber wall of sulfite pulp is more strongly dyed than the outer. In zinc chloride-iodine solution the sulfite fibers show a characteristic variation.

### FERROMANGANESE MANUFACTURE IN SPAIN

There is a note in the *Boletin Oficial de Minas* by the engineer of the district of Vizcaya saying that for the refining of the 294,000 tons of steel produced, 3,000 tons of ferromanganese are required. The article formerly was imported from abroad, but the extraordinary rise in the price of this product from 312 pesetas per ton in the year 1913 to over 2,000 pesetas at present and the almost insuperable sea transport difficulties have made it indispensable to have it produced in Spain and the necessary furnaces and engineering plants have been provided for the purpose.

#### ELECTRIC LAMP INDUSTRY IN FRANCE

In a recent communication to the Bulletin of the Société Interaationale des Electriciens, Mr. A. Larnande remarks that the present capacity of French glow-lamp factories amounts to 15-20 million lamps per annum, but this figure may be doubled in the near future. The tonnage required for the transport of material in this industry is small, as one ton of ore will provide sufficient material for 3,000,000 lamps. An important element in the manufacture of gas-filled lamps has been the production of argon required for the smaller types. This gas is now being made in considerable quantity by the process of Mr. Claude.

#### GERMAN ENTERPRISE IN THE UKRAINE

The firm of Krupp, says Engineering, is usually ready to step in where there appears to be a chance of a business worth doing. Its latest move is the formation of a concern with a capital of \$5,000,000 and an additional guaranteed capital of \$16,000,000 for the purpose of exploiting Ukraine industrially. A number of undertakings in the iron and steel industry in the machinery and electrical branch are also interested in the venture. At the same time, a number of banks and financiers have formed a syndicate for the exploitation of Ukraine financially and, it is added, in the matter of railway construction. The latter concern has so far a capital of only \$1,000,000 and its works will, in the first instance, be confined to a close study of the country and the possibilities it offers. The fact that the two concerns have not joined hands has caused some surprise, but the reason is stated to be that the banks wanted a concern which comprised all industries and did not find it expedient to coöperate with one which only represented a limited number. The two undertakings are understood not to clash in their Ukraine ventures.

### ANNEALING ALUMINUM

At a recent meeting of the Institute of Metals held in London, Mr. R. J. Anderson, in a paper on the above subject, urged consideration of the possibility of abbreviated exposure at various temperatures being able to confer workable properties upon cold-rolled aluminum sheet, with less fuel, in a shorter time, and with a smaller percentage of defectives in subsequent drawing. He gave particulars of a number of experiments in which various gauges of cold-rolled aluminum sheet were exposed for three minutes at a series of temperatures varying from 400° to 500° C. He concluded that exposure to 370° C. for 24 hrs., as is usual in commercial mill practice, is unnecessary, and that the lighter gauges can be softened by such an abbreviated exposure as three minutes at 400° C. He stated that tests in the mill have demonstrated that aluminum softened by short exposures to heat fulfils the draw-press requirements and that the percentage of defective shapes is smaller than with similar metal annealed for, say, 24 hrs. at 370° C. In the manipulation of certain shapes by the draw-press the sheet is ordinarily cut into circles or other geometric patterns and annealed before being drawn and, in one instance, the number of defective shapes was observed to be 30 per cent out of 4,400 blanks drawn, the metal having been annealed by long exposure. As a test of the effectiveness of long annealing, 200 cold-rolled No. 22gauge circles were annealed for three minutes at 475° and drawn by a typical draw-press operation into a given shape; only one defective shape resulted from rupture in the press, or a scrap loss of 0.5 per cent. Other tests on sheets of various gauges which had been annealed for relatively short times, ranging from 5 to 60 min., gave scrap losses of less than one per cent in all cases. He pointed out, that, if the annealing can be effected by relatively short exposures, a continuous annealing furnace for aluminum becomes possible, provided certain minor details can be overcome.

## TANNING MATERIAL IN GERMANY

The German Government, according to the *Chemical Trade Journal*, is offering prizes for the solution of the following three problems:

(1) A method for the currying and dressing of leather without the use of cod oil and other fish oils, as these oils are almost unobtainable.

(2) A substitute for chrome salts for the production of leather of the nature of chrome-tanned leather, also a substitute for the production of leather by means of other mineral salts or mineral salts combined with vegetable material which will produce a leather similar to combination-tanned leather.

(3) A method that can be used during the war which will result in a saving of vegetable tanning material without affecting the quality of the leather so produced.

A first prize of \$5,000 and a second prize of \$1,250 are offered in these cases. The offer is an indication that Germany is badly suffering from a lack of fish oils and grease for stuffing leather and from a shortage of chrome salts and vegetable tanning materials. The judges include Prof. E. Fischer, Dr. Fahrion, the oil chemist, Prof. Paeffler, a leather trade chemist, and five tanners.

#### JAPANESE CAMPHOR

The manufacture of camphor in Japan proper and Formosa during the fiscal year ending March 31, 1918, amounted to 10,678,800 lbs., of which 10,362,000 lbs. were sold by the camphor monopoly office. The latter figure shows a decrease of 4,989,600 lbs., as compared with the preceding year. The monopoly office has received many offers from Europe and America, but is unable to execute all because of the growing demand for camphor on the domestic market. Of 10,362,000 lbs. sold by the monopoly office, 4,276,800 lbs. were supplied to camphor manufacturing companies, 831,600 lbs. to celluloid companies, while 343,200 lbs. were placed on the market. The remainder, 4,910,400 lbs., were shipped abroad. The authorities, says the Chemical Trade Journal, are now encouraging the export of manufactured goods and preventing the shipment of camphor as far as possible.

#### NICKEL STEEL

In a recent issue of the *Elektrotechnische Zeitschrift* it is stated that the magnetic properties of nickel steel caused it to be used by the German navy for the construction of parts of ships near to the compass in order to prevent variable effects on the compass field. It has, however, recently been stated in the same journal that this use of nickel steel is by no means new and, in fact, is a very costly method of obtaining good compass fields. On this account the method has been almost completely discontinued. The compasses are now almost entirely gyroscopic. The use of this type of compass has the further advantage of saving large quantities of nickel which is so expensive and difficult to obtain.

#### GAS-FIRED BRAZING TABLE

A self-contained, gas-fired brazing table designed by the Davis Furnace Company, Luton, England, especially for the aeroplane industry and certain toolmakers' work, has a firebrick table 3 ft. 10 in. by 1 ft. 6 in., mounted on a strong cast iron stand. There are two blowpipes, 19 in. long with  $^{7}/_{16}$  in. nozzles and 1 in. heads, each swivel-mounted on a vertical pillar with suitable adjustment for height. For lateral adjustment the pillars slide along a machined bar of square section fixed horizontally along the front of the table. The air-blast is provided by a high pressure blower mounted on a shelf below the table and driven by belt or by electric motor. The gas and air are conveyed to the blowpipe by flexible metallic tubes, each with its separate main control cock.

## A CHINESE PERFUME PLANT

The plant locally known as Lang-rhoa (*Cymbridium ensifolium*), one of the finest orchids known, is regarded in China as the queen of flowers. An account of its cultivation has recently been published by Yang-Tsen Kia, as its scent is so exquisite that it holds great possibilities for the perfume industry. So valued is this plant that the greatest care and attention are devoted to its cultivation. Each plant is grown in a separate pot, the temperature during the day being maintained at 17° to 20° C. and during the night at 12° to 14° C. Ventilation must be abundant and only rain water used for watering. The perfume is very powerful and very sweet and it is possible that the essential oil may be distilled from the plant, when it would become available to European perfumers.

#### THE SCHOOP METAL-SPRAYING PROCESS

From Zurich comes the news of considerable improvement in the Schoop spraying process, says *Engineering*. Instead of melting the metal, which is generally applied in the shape of wire by the oxyhydrogen flame or the blow-pipe, electric fusion is now used and is said to be both simpler and cheaper. The pistol apparatus is used as before, but two ends of the wire are placed in the pistol instead of one and they are approached to one another as electrodes of an electric circuit. When the arc strikes, the wire fuses and the air current tears the fine metallic particles away. Zinc sprays in particular have been produced in this way, according to an article in *Z. angew*. *Chem*. The electric heating may be simple, but the prevention of the oxidation of the sprayed metal will probably be as difficult as before.

## NEW SOURCE OF ALCOHOL

Among the substitutes for fibrous material to which German manufacturers have been compelled to have resource is the black millet (*Sorghum vulgare*). It has found a place in paper making and it is now suggested as a material for the production of alcohol. The food value of the grain is high, between that of peas and lentils, so that its cultivation, which costs no more than that of wheat or rye, is recommended to the farmer on the ground of its being a paying crop. If the straw be used as a source of cellulose or of alcohol, the crop becomes doubly valuable.

## BICHROMATE MANUFACTURE IN SWEDEN

The British Commissioner at Stockholm reports that a large new factory has just been started at Malmo for the production of bichromate, chrome alum, and other chromium salts. The undertaking has been financed by Swedish and Danish interests and the proposed scale of operation is sufficiently great to render importation of these materials unnecessary. Hitherto these have been imported from Germany and the United Kingdom to the value of \$1,220,000 per annum.

### BEECHNUT OIL IN THE NETHERLANDS

The Dutch Minister of Agriculture, Industry. and Commerce plans to increase the supply of edible oils in the Netherlands by using the domestic beechnut crop. He estimates that between 2000 and 2500 metric tons of these nuts can be collected and that this amount of raw nuts will yield 300,000 to 400,000 kilos of oil, a valuable addition to the dwindling stocks of edible oils in the Netherlands. The *Zutphen Gazette* reports that school children are to be used to gather the nuts. Owners of private lands on which beechnuts are gathered will receive 5 per cent of the sums paid to the gatherers and will have the right to purchase cattle cake prepared from the pulp of the nuts from their own property.

## SCIENTIFIC SOCIETIES

## FRENCH SECTION, AMERICAN CHEMICAL SOCIETY

Chemical Warfare Service A. P. O. No. 717, American E. F. October 21, 1918

### DEAR DOCTOR HERTY:

I know that the members of the AMERICAN CHEMICAL SOCIETY will be interested in the following communication from Prof. V. Grignard. The letter is self-explanatory.

Ministere de l'Armement et des Fabrications de Guerre

Inspection des Études et Expériences Chimiques

MY DEAR COLONEL:

## Paris, September 28, 1918

Allow me to acknowledge with thanks the receipt of the documents which you sent to my laboratory: Doctor Parsons' letter to you, including membership blanks for the AMERICAN CHEMI-CAL SOCIETY, and the charter which was granted by that Society for the formation of a French Section.

I can assure you that French chemists will welcome the opportunity to cultivate advantageous relations with their American colleagues, and I am convinced that the French Section of the A. C. S. will shortly become a worthy complement to the American Section of the Société de Chimie Industrielle.

I feel deeply honored by the privilege of transmitting the charter to the new Section, and I shall do everything in my power to further this matter.

With sincere regards, believe me to be,

Most cordially yours,

V. GRIGNARD, Directeur

LABORATOIRE CHIMIQUE MILITAIRE DE LA SORBONNE 1

We are all extremely busy just now, but arrangements have been made whereby the French Section of the AMERICAN CHEMI-CAL SOCIETY will be formally organized.

Our colleagues at home will also appreciate this note from M. Landowski, President of the Société des Chimistes Français, of which the General Secretary is M. Arpin, and the Treasurer, G. Sellier.

#### Société des Chimistes Français

#### Paris, July 4, 1918

COLONEL:

At this solemn hour, when all France, as a single soul, proclaims her eternal gratitude to the Sister Republic whose citizens have unanimously responded to the call of their immortal President by coming to the aid of Right and Liberty, the Société des Chimistes Français, recognizing the importance of the rôle played by chemists in the liberation of the world, wishes to transmit, through the Chief of the Chemical Warfare Service of the American Army, fraternal greetings and an expression of its admiration for all American chemists who have placed their learning and their lives at the service of liberty.

Receive, Colonel, the assurance of my very highest regards, The President,

T

H. LANDOWSKI

With kindest regards from Major Hamor and myself,

## Cordially yours,

R. P. BACON, Colonel, C. W. S. Chief of Technical Division

## IOTA SIGMA PI

The first national convention of the Iota Sigma Pi, an honorary chemical society for women, was held at the University of Nebraska, Lincoln, Nebraska, in the new Chemistry Hall, just opened. Five of the eight chapters which constitute the fraternity at present were represented by delegates. The object of the Society is not to take the place of Sigma Xi, AMERICAN CHEMICAL SOCIETY, or any other organization, but is to foster and stimulate interest in chemistry among college women and to advance the standard of personal accomplishment in chemical fields, thus making the work of women in science more effective.

The spirit of the society may perhaps be best illustrated by quoting a few suggestions made by the National Convention:

I—In view of the present emergency, the Convention recommends that every member of Iota Sigma Pi encourage all young women to train themselves for scientific work.

2—In order to further the ideals of this organization the Convention recommends that every member, as soon as she is able, join the AMERICAN CHEMICAL SOCIETY.

The national officers elected were as follows:

President: Mary L. Fossler, Nitrogen Chapter, University of Nebraska. Vice-President: Miriam E. Simpson, Hydrogen Chapter, University of California.

Secretary: Edith Hindman, Oxygen Chapter, University of Washington.

Treasurer: Icie Macey, Tungsten Chapter, University of Colorado. Editor: Helen Keith, Iodine Chapter, University of Illinois.

A directory of the Society is in the process of preparation and will be sent out to each Chapter when completed. Bulletins will also be sent out from time to time by the Editor.

#### SOCIETY OF CHEMICAL INDUSTRY NEW YORK SECTION

At the meeting held in Rumford Hall on Friday evening, October 25, 1918, Major W. H. Dudley of the British-American Anti-Gas Liaison Office spoke on "Gas Warfare both Offensive and Defensive." Having already printed the address of S. J. M. Auld on "Methods of Gas Warfare,"<sup>1</sup> covering more or less the same ground, we do not give Major Dudley's address in full; but because of the interest of the explanations they contain, his introductory remarks are given here.

It is now a matter of common knowledge that the Germans introduced the use of asphyxiating gases in warfare by launching clouds of chlorine gas against the unsuspecting and unprepared Allies in the neighborhood of Ypres on April 22, 1915. In spite of this well-established fact they have from time to time attempted to saddle the Allies with the responsibility of having started this latest horror of modern warfare. On July 17, 1918, their official wireless sent out a communiqué to this end. This wireless message stated that "the idea of using poison gas originated with the British Admiral Dundonald."

The Admiral Dundonald to whom reference is here made is probably an Admiral of that name who was born in 1775 and died in 1860. He was a man of considerable chemical knowledge and warned the British Government of that date that it might be possible to employ asphyxiating gases in warfare. This possibility has, of course, been known to all the Great Powers, and because of this knowledge the Hague Convention of 1899 expressly forbade the use of gas. It remained for Germany deliberately to violate this stipulation in the early stages of the present war.

The German wireless message further states that "poison gases were first used in the war on March 1, 1915, by the British and French, whereas the French and British Army could not announce a German attack with poison gas until April 24, 1915." (The attack actually took place on April 22, 1915.) This statement is a deliberate lie and will not bear examination. It would mean that in a period of about eight weeks the Germans developed sufficient material in organization to carry out an extensive gas attack. This is an absolute impossibility.

The best answer to this typical German falsehood is given in the words of Lord French, who, as Commander in Chief of the British Army at the time, in his report of May 3, 1915, stated as follows: "A week before the Germans used this method (gas attack) they announced in their official communiqué that we were making use of asphyxiating gases. At that time there appeared to be no reason for this astounding falsehood but

<sup>1</sup> THIS JOURNAL, 10 (1918), 297.

now, of course, it is obvious that it was part of the scheme. It shows that they recognized its illegality and were anxious to forestall neutral and possibly domestic criticism."

It is interesting to realize that as late as July of this year the Germans should still be attempting in a most unscrupulous way to place the responsibility of initiating gas warfare to the account of the British and French.

At this meeting the Section unanimously adopted the following resolution:

WHEREAS, for many years the German Government has fostered the chemical and other "key industries" with the object of reducing other nations to dependency upon her, and at the same time rendering herself independent of others, and establishing industries which in time of war would give her an enormous advantage over those she was planning to attack and rob; and

WHEREAS, from the very beginning of her outrageous attack upon the civilized nations of the world, Germany has pursued a deliberately organized course, having for its object the permanent economic injury or destruction of other countries who had been her competitors in the world markets; and

WHEREAS, in pursuance of this course Germany has deliberately

First: Stolen and carried away whatever machinery she could;

Second: Destroyed whatever machinery and property she could not steal or carry away;

Third: Deported or destroyed communities of skilled artisans;

Fourth: Murdered or by studied brutal ill treatment permanently injured prisoners of war and innocent civilians, so as to deprive their countries of their skill and labor; and

WHEREAS, it is essential that the allied civilized nations must, as a matter of self-protection, render Germany impotent to do further harm from a commercial as well as from a military standpoint, and prevent her, although defeated on the field of battle, from reaping a commercial triumph as the result of her deliberate wickedness above referred to;

Therefore be it Resolved, that the New York Section of the Society of Chemical Industry requests that the proper authorities of the various allied governments take special note of the above facts, and insist that Germany, where possible, be compelled to restore the stolen machinery and other property, or replace the stolen property and also whatever machinery or property has been destroyed by equivalent machinery or property taken from German factories; and that they furthermore see to it that all allied industries are fairly and justly safeguarded under the ultimate terms of peace, against the machinations of an insidious and conscienceless enemy, whose express intention is to reduce other nations to industrial subservience and dependence.

## NOTES AND CORRESPONDENCE

#### AN OPPORTUNITY TO HELP THE FRENCH

A communication has been received from the chairman of the American Ouvroir Funds, 681 Fifth Avenue, New York City, asking the AMERICAN CHEMICAL SOCIETY to interest itself in securing among our members the "adoption" of children whose fathers were technical men and who have been orphaned by the death of their fathers, graduates of l'École Polytechnique who have fallen at the front.

In using the word "adoption" it is not, of course, intended to bring the children to this country and immediately adopt them, but to help the officers' widows educate their children and bring them up as nearly as possible as would have been done had their fathers lived. L'École Polytechnique has among its graduates some of the most illustrious, brilliant, and educated men in the French Army. Many of them were poor and are among those whose families now most need help. Although America has lost many men on the French front, they have, with few exceptions, been young men without dependents; so that we shall not realize in our own country the great need which has come to France where the families in many cases have been left entirely dependent.

The American Ouvroir Funds will be glad to submit to any responsible man or woman who requests it, a selection of histories of these technical graduates, with photographs of the war orphans, the citations of their fathers, their addresses, and all the facts which may be of interest to anyone who may "adopt" them. "Adoption" means an annual expenditure of from \$100 to \$250 a year, according to the circumstances of the family whose child is "adopted." Such expenditure will insure board, lodging, and education for a child whose father has been killed in the war.

The following is taken from a communication sent to the Secretary by the American Ouvroir Funds:

#### SAVING CHILDREN FOR THE FRANCE OF TO-MORROW

In the midst of the overtaxing burdens of war, men and women of France, with international reputations for achievement and character, have found a way, in spite of the thousands of orphaned children, to give a personal accounting of individual cases. These men and women are associated with various French Societies long established for the care of orphans.

The American Ouvroir Funds as the chosen link with America of these well-established organizations in France, stands for the French idea of personal service and contact. It asks for a definite sum for an individual orphan, whose story one may have, whose photograph may be seen, to whom one may write, from whom letters will be received. No personal gift contributed as an individual fund through the American Ouvroir Funds is lost in the great melting pot of war benevolence. It goes straight from you, bearing your message of sympathy, and brings directly back to you a warm response from the heart of a child or its mother. What a glorious privilege for us to be able to help preserve to these children their precious heritage; to give as nearly as possible to them the same chance for environment and education that would have been theirs had their fathers lived. We give with some understanding of the varying individualities and circumstances of the orphaned children. Our aim is not just to clothe and feed a quantity, but to pre-

Our aim is not just to clothe and feed a quantity, but to preserve to France, the children of the men who in every rank of life represented what was most noble, most worthy, and most high-minded in their country.

We reward a brave soldier who has died fighting for the cause of individual liberty, of America as well as of France, by giving the aid that is necessary to keep his child out of an institution and under the protection of the mother or some loving guardian; to be brought up in his own faith and to the same opportunities that would have been his had the free life of France been uninterrupted by war.

France asks nothing of the world. She fights, has fought from the beginning of this war, with her eyes to the front, her head lifted proudly in the assurance of the righteousness of her cause. She says nothing of what she has endured, utters no outcry for the needs of her people. France is proud. But we who look on must see those scars, must see the needs of her orphaned children, and, since she is fighting for America's cause also, they should be as our orphans.

We owe it to her that her children at least should not suffer, should not lose, as the result of their father's sacrifice, one jot of that individuality, that freedom, which is the priceless heritage of their country.

The above was brought before the Advisory Board of the AMERICAN CHEMICAL SOCIETY at its recent meeting in New York. The Secretary was instructed to inform the members through THIS JOURNAL. "Adoption" can be made by a number of individuals as well as by one individual, if necessary.

President and Mrs. Nichols have "adopted" the first two, a boy and a girl. Four others are promised. You will be put in personal touch with the child you "adopt."

Many American citizens, both men and women, have welcomed the opportunity thus offered to relieve in some measure the burden of the war that has fallen on the women and children of France. The informal "adoption" of one or more of these little children entails no obligation other than a contribution to the child's maintenance for one year.

It puts the adopter into immediate personal relations with

a French family, and brings the joy of helping a little child to become a worthy citizen of France.

The several French Societies transmit the full amount received for the children, without deduction for expenses or cost of any kind.

Local sections will please take up this matter. Members may send to the Secretary, who will either choose for them or secure the photographs of the children and history of the family helped.

CHARLES L. PARSONS, Secretary

## NEW AFTER-WAR PREPARATIONS IN THE CHEMICAL INDUSTRY OF GERMANY<sup>1</sup>

THE AGREEMENT BETWEEN THE DYESTUFF TRUST AND THE CARTEL OF EXPLOSIVES. REDUCTION OF THE TAX ON WAR PROFITS IN FAVOR OF PRODUCTS MANU-FACTURED FOR EXPORT. THE NEED FOR AN INTERALLIED TECHNICAL ORGANIZATION.

The organization which has been called the German Dyestuff Trust is already old; but recently its development has been completed by an agreement with the Cartel of Powders and Explosives. This latter, before the war, was controlled by the Nobel Trust Co. of London, but at the end of 1915 elimination of the English company was effected by an exchange of the German shares which it owned for English stock held by German firms. The Cartel of Powders and Explosives then comprised only houses of German nationality whose nominal capital represented a total of about 100 million marks. At the present moment, however, the financial strength of the group is considerably greater; the profits made, the reserves established, and the enlargement of plants are all proofs. In fact, during the war, such factories as the Bayer and Badische have produced almost exclusively explosives, gases, and acids, and these have been furnished as raw materials to companies manufacturing powders and explosives. Hence the two cartels which have concluded an agreement have an output of very similar products. There is no doubt that the installations made and developed for the manufacture of explosives, gases, and munitions will be maintained as they are, ready to function from the start of the next war. Therein lies an urgent counsel of M. Rathenau, and German technicians declare on every occasion that never before did they begin a war with such an inferior industrial organization, that it is necessary to be better prepared for the next one-a provision for the future which will not prevent them from employing, in the meantime, the factories and materials in the manufacture of chemical and pharmaceutical products, synthetic perfumes, etc. Thus, the aim and object of the organization of the Dyestuff Trust is to give its directors the mastery of trade, domestic and foreign; it is to preserve this that the Trust has concluded an agreement with the Cartel of Explosives.

Accordingly there is now in Germany a single concern selling dyestuffs, chemical and pharmaceutical products, a single purchaser of prime materials for these industries, and this Trust is already assured of the ownership or control of several lignite mines of importance. This concentration should permit the reduction to a minimum of the cost price and the fixing of export sales prices at a figure which will enable products to pass over tariff barriers. Preparations for beginning exports when hostilities have ceased are complete, reaching the point where the merchandise is already packed and labelled, either in French or English, while catalogues in both languages have already been printed.

But the efforts made in Great Britain and France to establish and develop the dye industry and manufacture of organic products, the rapid and unexpected development of this industry in the United States and in Switzerland, have caused a feeling of uneasiness in the Trust, and also, in the Imperial Government, which considers dyes to be one of its best economic weap-

<sup>1</sup> Translation of an article in Chimie et Industrie for June 1, 1918.

ons. Even those who rely on a free trade restocking Germany with raw materials, in view even of guarantees in this respect in the future treaty of peace, even these men cannot be ignorant of the fact that in many foreign countries German products will meet with hostility which no text of treaty will be able to prevent. Hence they proclaim the necessity of still greater production and at a lower price. The particular interest which the Imperial Government takes in the dye industry has probably still another cause due to the knowledge that it has become the stockholder and associate of the great companies such as the Bayer, the Badische, etc.

When it became necessary to enlarge the existing works and to establish new factories equal to the task of making munition of war, the State made the considerable advances of money required, because the times were pressing, and it was impossible to think of increasing the capital of the companies. At the end of 1917, the majority of the firms belonging to the Trust had increased the capital of their concerns 150 million marks in round figures, the flotation of the new stock to take effect January 1, 1918. It is to be noted, however, that the Bayer and Badische companies each asked for the listing on the Berlin stock exchange of 18 millions of new stock and not 36 millions. the amount actually issued. Similarly, the Gesellschaft für Anilinfabriken issued 12 millions and asked for the listing of only 5.8 million marks. In view of the debt contracted by these companies with the State and the zeal of the latter for the interests of the public treasury, the natural conclusion is that the repaying of the sums advanced by the Empire was effected by remittance of new stock, which, of course, was not admitted to dealings on the Bourse. The result is that the Empire has made an excellent investment (the last dividend of the Badische was 25 per cent), it will be represented on the boards of directors, and becomes directly interested in the prosperity of these companies. They are now certain that all the powers of the government will be exerted in their favor.

The first result of this association is that, from this moment the Imperial Government will grant the remittance of a large part of the tax on war profits to the manufacturers of dyestuffs and chemical and pharmaceutical products which are actually being made for export as soon as hostilities have ceased.

Under such conditions the chemical industry of the enemy will be in a position to produce merchandise of various kinds at a price which costs the manufacturers nothing. From the first day of peace they will export this merchandise and will be able to deliver it in Great Britain, France, Switzerland, Italy, and the United States at a price which will not represent even the customs duties, however high, imposed by these different countries. The budding industries of the Entente nations will thus be placed in a position in which it is impossible to live, and their competition so much feared by the enemy will be killed in the germ. The Germany monopoly once reconstituted and become definite in aim, cost prices which are remunerative will be fixed, and the products of its chemical industry will again serve as excellent articles of "compensation" to obtain favorable treatment for other merchandise.

We must not deceive ourselves as to the grave danger presented by this Machiavellian combination, especially for France, Great Britain, and Italy, for in Switzerland and in the United States the dyestuff industry is more developed, while the United States possesses raw materials as compensation, such as copper and cotton, which will afford the means of an economic struggle. But in France and Great Britain it is scarcely likely that manufacturers will be in a position to supply the necessary dyes and pharmaceutical products when peace is made. Industries which utilize dyestuffs will find themselves in the presence of German offers, ready for delivery at an extremely low price, whereas British and French firms will have, in the case of many articles of manufacture, only promises or very high prices. It is more than doubtful whether a considerable number of these consumers will postpone business activity until the moment when they will be able to obtain the products of national industry. In every way all possibility of exportation will be extinguished, Germany having recaptured her clientele in every country where chemical industry has not been solidly established.

In France and Great Britain men are strongly individualistic and opposed to concentrations of industry; we talk readily of good relations between commercial houses or the laboratories, but the bonds between factories remain loose for the most part, and those between companies belonging to different countries are far more relaxed. In face of the German Trust which, thanks to its organization, can sell at any price whatever, it is to be feared that there are concerns of more or less financial strength, several of which will manufacture the same article and will perhaps compete with each other while other articles of merchandise will be lacking. In this case tariffs are not a remedy, for duties, however high, will be powerless to prevent the penetration of articles which the Germans will be able to sell at an insignificant price and which cannot be supplied by other countries. We wish to point out that, in relying on high tariffs, we may be mistaken, while their establishment against neutrals will raise grave difficulties. It is well known that, for this reason, the intervention of neutrals is part of the German program.

Does this mean that we must be resigned, or expect everything from the prohibition of imports of enemy chemical products? Certainly not, but it is necessary to resort to energetic measures, however rigorous they may appear to our habits of independence and liberty.

The first thing to realize is the methodical re-allotment of labor and the specialization of manufactures in the countries of the Entente. For this purpose it would suffice if, in these countries, the entire group of corporations which manufacture dyestuffs, pharmaceutical products and derivatives were in agreement to accept a central committee of technical directors. This committee, knowing the needs of each country and versed in the material and technical resources of its works and factories, would introduce a special organization into each, of such a kind that each product would be manufactured by one or two works, which would permit the most economical production and an output nearest to the centers of demand. The same technical committee would effect likewise a specialization of the munition factories before they are used for after-war purposes. Under these conditions the business and administrative freedom of all these companies would remain untouched, but the technical direction would be the work of one board-a system which implies the minimum of interference with the life of the most individualistic of concerns. The technical committee would all be experts trained to receive the communication of researches made in the laboratories and to indicate those which appear to them useful. It would seem that with such an organization our manufacturers might arrive at a point where they could make themselves independent of Germany in the matter of nearly all the products which she counts upon supplying at the end of hostilities, either directly or by the intermediary of a borrowed neutral name. Then custom duties might be raised until they reached a prohibitive level.

Measures of this order certainly constitute an assault on the independence of corporations, but it must not be forgotten that it is a question of life or death for our infant chemical industry; it was permissible, in a rigorous sense, to hope for success in face of the German trust, but before the perspective of a combine which will permit the enemy to make a pretense of renouncing dumping, under the guise of selling for almost nothing, the struggle of isolated industries becomes impossible, and hence a technical organization is a necessity, we may even say, a duty.

## R. PETIT Professor of the Faculty of Sciences of Nancy

## THE AMERICAN DYESTUFF INDUSTRY AND ITS PROSPECTS<sup>1</sup>

With the advent of 1918 the American chemical works, and especially the dyestuff factories, were confronted with numerous problems. Owing to the requirements of home and Allied industries they found themselves in a difficult position, for, despite all promises, they were not able to command a sufficient, nor even a moderately satisfactory supply of the most important fundamental materials. Americans, induced by the promises of company promoters, and with an eye to great expansion of the markets, have invested, since the outbreak of the war, about 225 million dollars in dye works, and yet, as they expressly give out, have produced only dyes which hitherto have been made only in Germany. How much of this vast sum has been actually paid in, it is not possible to judge, but it may be admitted that the companies are very much "watered." In order to provide security for this capital, those interested clamor for a protective tariff, by which, after the war, they are to be preserved from a destroying competition. The interested circles point out that war requirements have diminished stocks of raw materials throughout the world, so that the prices of dyestuffs and technical chemicals even after the war will hold at an abnormal figure. The same circles trot out the old fable according to which Germany has accumulated important quantities of dyestuffs and chemicals with which to inundate the world's markets after the war. Experts, however, with keener insight, do not support this view, suspecting that Germany herself has experienced a certain shortage of raw materials for this purpose. The greatest concern of the American producer is the fear that, after the war, Germany will purchase large quantities of raw materials in the United States. Although the industry has a specious appearance, as if some of the leading factories had achieved a fair amount of success in making some products, the position of a portion of the industry is regarded as insecure, and even as distinctly a hazard. A feeling of decided irritation was observable when the Government in 1917 commandeered all supplies of methyl alcohol at a fixed price, since methyl alcohol forms the basis of many dyestuffs. At the same time the Government took over the entire output of toluol, and all gas companies were required to set up ovens for the preparation of tar products. In spite of the efforts of the dye manufacturers, consumers complain that the prices of dyes are still very unfairly differentiated from those existing before the war. In addition to this, the quality of the dyes, in the judgment of the textile industry, leaves much to be desired; the textile products, especially for military purposes, are not satisfactory, as their fastness to light and water is uncertain.

The general opinion is that, so long as no foreign competition breaks down its development, the American dye industry may well be in a position to satisfy a demand restricted by defects of quality and fastness. But in its present proportions the American industry has not grown up to the demands of fashion and of other individual consumers, so that its development in 1918 will run in the grooves of the past year, and this means that only staple dyes without much variety will be produced.

## THE JOURNALS OF THE AMERICAN CHEMICAL SOCIETY

#### Editor of the Journal of Industrial and Engineering Chemistry:

It has often occurred to the writer that the journals of the AMERICAN CHEMICAL SOCIETY show a peculiar dissimilarity in the headings of the solid pages of reading matter, and might possibly with slight changes be made a little more convenient for one using them in reference. Presumably the present arrangement follows custom or precedent and is designed to

<sup>1</sup> Translation of an article reprinted in the Zeitschrift für angewandte Chemie, March 19, 1918, from the Norddeutsche Allgemeine Zeitung.

give a balanced and neat appearance to the page, but probably none of us will mind sacrificing a little in this respect, if necessary, if there is a compensating advantage in using the journals.

The Journal of Industrial and Engineering Chemistry carries on the left-hand page of reading matter its own name, the volume, and number; on the right, the date and its name again. The Journal of the American Chemical Society has on the left the name of the author, and on the right the subject of the article. Chemical Abstracts has the name of the journal on the left and the branch of chemistry on the right.

Without going too far into specific suggestions, the writer would like to see the headings of the pages arranged so that one can get as far as possible the references without, for example, turning back to the front cover to find the volume number each time, and then perhaps having to translate a Roman numeral. There is little difference in looking up one or two references, but for a larger number it is distinctly easier to use the Journal of Industrial and Engineering Chemistry than either of the others. Even the addition of the volume number to the pages of the other two journals would be a real convenience. Without expanding too far, the point to be emphasized is the rather strange dissimilarity of headings, each of which has a part, but only a part, of the essential data used in index or reference work. Could we not with little effort modify our headings to fall in with the present spirit of efficiency and at the same time answer all the practical and esthetic requirements of the printed page?

WEST DULUTH, MINN. October, 28, 1918

Pl

CHAS. F. GOLDTHWAIT

#### THEFT OF PLATINUM

The following notice has been sent us by Mr. G. D. Buckner, chemist of the Kentucky Agricultural Experiment Station:

#### \$100.00 REWARD

For the recovery of the platinum dishes and crucibles answering the following descriptions stolen from the Kentucky Agricultural Experiment Station, Lexington, Kentucky, during the week following October 17, 1918, or for information leading to the conviction of the thief:

latinum		Platinum	
Dish	Weight	Crucible	Weight
No.	Grams	No.	Grams
2	11.9750	1	46.4689
3		11	32.6709
10	16.0273	12	33.0927
	8.4319	14	49.1097
	15.8232	15	48.6788
	15.7905	20	48.5347
	15.7580	22	48.3856
	18.9421	23	47.2223

The urgent need for this material at this time deserves your earnest effort and coöperation in its recovery. Address J. J. Reagan, Chief of Police, Lexington, Ky.

#### CHEMICALS FOR RESEARCH WORK

## Editor of the Journal of Industrial and Engineering Chemistry:

In your issue of August r you were good enough to insert a letter announcing that the Research Laboratory of the Eastman Kodak Company were undertaking the preparation of chemicals for research work, and asking the coöperation of the manufacturers of intermediate products and of organic chemists either in the industries or the universities who were preparing materials which might be of use to others or who had need of organic reagents. As a result of that letter and of the endorsement of the sections of organic and industrial chemistry at the Cleveland meeting of the AMERICAN CHEMICAL SOCIETY we have received a great deal of assistance and feel most grateful to the chemists of the United States for the hearty response which they have given to our request. The manufacturing concerns have proved willing to supply us with the various raw materials and intermediates which they produce, and a considerable number of university and other research chemists have written to us offering their assistance in preparations.

A special department of the Research Laboratory has now been established under the name of the "Department of Synthetic Chemistry," and has been staffed with women chemists, who are proving most enthusiastic and capable in this work.

Up to the present time we have not found it possible to issue a list of the chemicals which are available, though a considerable number are now in stock on our shelves. The University of Illinois has supplied us with the chemicals which it prepares. We have already obtained a few from other sources. We have prepared a number of new reagents ourselves, and we are engaged in the purification of a number of intermediates, some of which are purified with ease, while in the case of others the process of purification is proving extremely difficult and expensive. We hope to issue our first price list of chemicals by the first of December and shall be glad to receive applications for copies of this price list when issued. At first it will probably be necessary to issue new price lists monthly, adding reagents as they become available.

It is our purpose to stock chemicals eventually of three grades of purity. The first class will embrace chemicals only of the highest purity which it is possible to obtain, and we propose to distinguish these by the name of "Eastman" chemicals. In our first list we shall include chiefly these chemicals of the highest purity, since the supply of these appears to be most urgent. The second class will be prepared of the purity necessary for the greater number of synthetic organic preparations. The amount of purification which the technical product must undergo will depend both on the technical product and on the reaction for which it is generally used, and the greatest care will be taken to see that the chemicals supplied under this class are really suitable for the purposes for which they are likely to be employed. We propose to state, as far as possible, their purity and the impurities which they contain. We shall distinguish these chemicals under the term of "Practical Synthetic" chemicals. The third class will consist of crude technical intermediates should there prove to be a demand for these, as we expect will be the case. In Germany these technical intermediates have been supplied by the firms who supply chemical reagents and for many purposes it is advantageous for chemists to be able to obtain them in small quantities. We find that the makers of intermediates would prefer that we should retail them rather than fill orders for small quantities of these materials themselves. We shall designate these "Technical" chemicals. In some cases the "Practical" and "Technical" products will naturally be identical.

Unless there is great objection shown to the course, we propose to sell chemicals by metric weights only, listing them by the hundred grams and kilogram. We believe that this will meet with the approval of the majority of chemists, although up to the present almost all orders have come in for pounds. We have dealt with this by handling an order for 1 lb. as if it were for 500 grams. If our action in this is not endorsed by our prospective customers we shall be willing to alter it if necessary.

In this undertaking we regard ourselves primarily as serving the chemists of the United States and especially the members of the AMERICAN CHEMICAL SOCIETY, and we shall most heartily welcome any criticisms or suggestions.

RESEARCH LABORATORY EASTMAN KODAK COMPANY November 11, 1918 C. E. K. MEES

## COOPERATION BETWEEN MANUFACTURERS AND UNIVERSITIES

## Editor of the Journal of Industrial and Engineering Chemistry:

We are building up a collection of analyzed samples of raw materials and intermediate and finished products of our typical chemical industries, and expect to use these specimens as practical material in our courses in quantitative and technical analysis.

It has been our experience that the work in analytical chemistry is greatly strengthened by the use of such material, but at present the time of most instructors is too occupied to devote the time necessary to make the analyses required to check the results of the students. The laboratories of many of our chemical manufacturers make such analyses as a matter of routine, and it would be a very helpful method of coöperation if they could turn over to us and to other universities laboratory samples together with their analytical data on the same. You have advocated a closer coöperation between the manufacturers and the universities and it appears to me that here is a chance for a definite service involving little extra work on the part of the works laboratory forces. Samples of one to two pounds are sufficient for a year's supply, and different samples of the same material are useful in diversifying the work of different students of the same class.

We shall be glad to pay the transportation charges. The standard samples issued by the Bureau of Standards are too expensive for general use and their range is too limited.

We shall be grateful for any aid you can give us in this matter and shall welcome any suggestions as to an efficient presentation in the proper quarters.

R. E. OESPER

Associate Professor of Analytical Chemistry UNIVERSITY OF CINCINNATI

CINCINNATI, OHIO October 15, 1918

## INVENTION PROBLEMS

The Invention Section of the General Staff of the United States Army has submitted to the War Committee of Technical Societies a list of seven problems requiring scientific and inventive talent for solution. Problem V is of chemical interest and is reprinted here.

#### PYROTECHNIC SMOKE SIGNALS

It is desired to secure, if possible, a suitable chemical substitute for Red Saxony Arsenic now used for the manufacture of Yellow Smoke Signals. The characteristics of such a chemical are that it should produce the effect required, that it should be procurable in large quantities, and that it should be perfectly stable in combination with other chemicals, such as potassium chlorate. The effect desired is a rather deep orange-yellow. There is no objection to the use of dyes should these give the effect required and be procurable in large quantities at a reasonable price.

A suitable formula for a Red Smoke Signal is also a desideratum. The effect required is a pronounced and positive shade of red. As in the case of the Yellow Smoke Signal, chemicals composing it should be readily procurable and should be stable. Since, however, the requirements for this signal are considerably smaller than for the Yellow Smoke Signal a greater latitude may be allowed in selecting slightly less readily available and higher priced material for this signal.

The smoke signals outlined above are displayed from rockets, Very cartridges, Viven-Bessiere cartridges and 35 mm. cartridges. The rockets now used by our forces weigh about 2 lbs. with an approximate length of 18 in. The V-B, Very cartridges, and 35 mm. cartridges have an average length of about 6 in. with a diameter, respectively, of 2 in., 25 mm., and 35 mm. The V-B cartridges are thrown from the rifle grenade discharger, and the Very cartridges and 35 mm. cartridges from the 25 mm. signal pistols.

Should any person accredited by the Inventions Board become interested in the two pistols outlined above, this office would be very glad to give all the information in its possession

would be very glad to give all the information in its possession. It should be noted that Auramine has already been tried as a dye for the Yellow Smoke Signal and that Paratoner has been used in the Red Smoke Signal.

All communications regarding this matter should be addressed to Inventions Section, General Staff, Army War College, Washington, D. C., Attention of Captain Scott.

## SAFETY OF TNT AS AN EXPLOSIVE

Editor of the Journal of Industrial and Engineering Chemistry:

There have been quite a few cases in this country where trinitrotoluol has exploded under conditions which would lead us to believe that it is not the safe explosive that it is ordinarily supposed to be in contradistinction to pieric acid which is known to form rather unstable compounds with metals.

I would like to call attention to the fact that it is perfectly possible for trinitrotoluol to contain highly nitrated phenolic derivatives which could form salts with metals, thereby rendering the trinitrotoluol very much more subject to outside influences than if it were absolutely pure. I remember in the ordinary manufacture of nitrotoluol some ten years ago, we often isolated from our sodium carbonate wash liquors notable amounts of a red crystalline body which, at that time, I identified as a sodium salt of one of the nitrophenols.

In my reading, I recently came across a confirmation of this in *Berichte*, **18**, p. 2668, *et seq.*, in an article by Nolting and Forel on an investigation of the six isomeric xylidenes. In speaking of the formation of the nitrophenolic bodies in the nitration of xylols on page 2670, he says (free translation):

If one treats crude nitrotoluol, as obtained in the factory by nitration with mixed acid, with soda, a similar solution is obtained from which by sufficient concentration, a red and yellow mass of crystals separates. I have investigated and found that it consists of the sodium salts of the two dinitro cresols (the 1-methyl, 3,5-nitro, 4-hydroxy; and the 1-methyl, 3,5-nitro, 2-hydroxy derivatives), about  $\frac{4}{5}$  being made up of the first mentioned. The dinitro cresols are formed, according to my idea, from cresol which can result during nitration by the oxidation of toluol by nitric acid or oxides of nitrogen. From the ordinarily formed 1,2,4- and 1,2,6-dinitro toluols, the above isomers cannot be formed. It might be possible that small amounts of 1,3,4,5- or 1,2,3,5-trinitrotoluols are formed which could go over, under the influence of alkali, into the corresponding dinitro cresols by replacement of the 2 or 4 nitro groups with hydroxyl, but this assumption seems to me to be improbable.

I am sending you this information for publication in the Journal as I believe it will be of considerable interest to all those manufacturing trinitrotoluol and that these facts will be certainly worth taking into consideration in the manufacture and handling of the material if they are not already clearly recognized.

RESEARCH DEPARTMENT	J. M. WEISS
THE BARRETT COMPANY	J. M. WE100
NEW YORK CITY	
November 7, 1918.	

#### WOMEN IN THE CHEMICAL INDUSTRIES OF ENGLAND

The British Ministry of Munitions has issued a circular containing a list of processes in which women are successfully employed in connection with the following industries:

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NOTE-The possibility of employing female labor on some of the operations scheduled herein depends on local circumstances such as lay-out of plant, locality, type of labor available, etc.

The operations here scheduled may, in general terms, be classified as follows:

A-Simple laboring operations.

B—Operations requiring care, intelligence, and, or, resourcefulness.

C-Skilled operations.

D—Dangerous operations or operations requiring resistance to unpleasant conditions, e. g., heat, dust, fumes, odor, etc.

The different sections of the chemical industry in which women are successfully employed, and the departments of each section, are as follows: NITRIC AC A-B A-B

- B-Tankhouse: Blowing steam through vats B-Tankhouse: Noting temperature of fermenting mash
- A-Tankhouse: General laboring B-Cooking house: Charging cookers with maize meal
- A-General laboring

B-Tankhouse: Charging tanks with mash

ALUM

ACETONE

- A-General laboring
- ALUMINUM SULFATE
- A-General laboring
- AMMONIA (concentrated) at Gas Works
- | B-All operations
- ANILINE SALTS
- A-General laboring
- BARIUM CHLORATE
  - A-Assisting in concentration and crystallization
  - A-Chipping out crystals with chisel and hammer
  - A-Crushing, drying, and packing
- BLEACH
- B-Making up lute, making cell heads, cleaning up, oiling bearings in electrolysis house
- BUTYL ALCOHOL
  - B-Attending mixer
  - B-Adding salt to alcohol
  - A-General laboring
- CAUSTIC SODA
- BD-Fusing caustic soda
- BD-Ladling fused caustic soda from melting pots and casting into stick form
- A-"Detaching," i. e., breaking up caustic in cooling trays with hammer
- BD-Packing powdered caustic; labelling tins
- A-General laboring
- ELECTROLYTIC PROCESSES
  - A-Making up lute
  - B-Making cell heads
  - B-Preparing cell diaphragms
  - B-Assisting in dismantling, repair, and assembly of cells
  - B-Attending cells
  - B-Attending switchboards
  - B-Regulating voltages
  - B-Recording switchboard readings
- ETHER CAMPHOR
- B—Final dressing and preparing of camphor tubes FERTILIZERS
- BD-Grinding slag in cake mill
- BD-Grinding phosphate in Kent mill
- AD-Mixing guano
- A-General laboring
- IODINE
- A-Screening salt in extraction of iodine from kelp
- LABORATORY
  - C-Research chemists
  - C-Routine testing
  - B-Laboratory attendants
  - C-Controlling chemical laboratory
  - C-Acting as chemist-in-charge
  - B-Assisting in making up culture-tubes
- C-Mounting organisms on slides and noting their condition
- MAGNESIUM SULFATE
  - B-Crushing magnesite
  - B—Charging dissolvers
  - B-Attending evaporators and crystallizing vats
  - B-Whizzing
- MAGNESIUM CARBONATE
- A-Discharging filter presses
- B-Packing presses for moulding
- MISCELLANEOUS
  - A-Helping on press for compressed sal ammoniac
  - B-Operating machine for tableting ammonium chloride
  - B-Control of acid circulation pumps
  - B-Assembling parts in drum-making shop
  - C-Control testing on plant
  - A-Feeding and attending dissolvers
  - B-Charging and discharging drying ovens
  - A-Assisting in repacking condensers and towers (ground work only)

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- B—Assisting in repairs to decomposers
- B-Controlling valves for blowing liquids from vats
- NITRIC ACID
  - A-Charging nitrate, attending and emptying rotary drier
  - B-Weighing charges of nitrate for stills
  - BD-Charging stills, luting manhole and pipe joints
  - B-Running on acid
  - BD-Firing still and controlling temperatures
  - B-Attending and greasing acid pumps

NITRIC ACID (concluded) A-Breaking dumped niter cake, barrowing, and tipping into barge A-Breaking up niter cake in cooling pans C-Sampling and testing AD-Filling, sealing, and packing carboys BD-Working on Valentiner nitric acid still A-General laboring OLEUM AB-Unloading pyrites, attending breaking machine AB-Hauling broken pyrites, weighing charges of pyrites on sulfur B-Charging and attending sulfur burners C-Sampling and testing AD-Grinding and calcining magnesium sulfate B-Impregnating granulated anhydrous magnesium sulfate with platinum chloride AD-Filling, sealing, and packing carboys A-General laboring PHENOL A-Washing and stencilling drums A-Unloading empty drums, testing, and stacking A-General laboring PHOSPHORUS AD-Finishing AD-Packing amorphous phosphorus REFINED BICARBONATE OF SODA A-General laboring REFINED SODA CRYSTALS A-Tipping soda ash into dissolvers B-Cleaning filter presses B-Filling, operating, and emptying centrifugal driers A-Grading crystals A-General laboring RESPIRATORS B-Operating press tools for stamping out frames on plates B-Mechanically cleaning same B-Dipping in acid B-Nickel plating B-Cleaning and polishing B-Mounting with tapes and elastic bands A-Packing SILICA A-Drying on open floors A-Crushing and bagging SILICATE OF SODA A-General laboring SODA ASH A-Charging vats with black ash A-General laboring B-Taking distiller temperatures SODIUM BISULFITE BD-Dissolving sulfur dioxide in caustic soda BD-Concentrating sodium bisulfite solution SODIUM (METALLIC) BD-Charging and dipping from electric furnaces SODIUM SULFIDE A-Stripping and breaking from detaching beds A-General laboring SULFUR A-Melting crude sulfur A-Breaking out sulfur from sulfur beds A-Emptying sublimers, dressing flowers of sulfur B-Preparing moulds for roll sulfur A-Removing from moulds after casting A-General laboring SULFURIC ACID A-Feeding and attending pyrites breaking machine A-Sieving pyrites B-Weighing out charges B-Charging furnace (or burners) C-Controlling valves on de-arsenicating plant

- AD-Filling and sealing and packing carboys
- C—Sampling and testing
- BD—Coking Kessler concentrators
- BD—Helping on cascade concentrators
- BD—Operating Gaillard tower concentrators
- B-Feeding Kessler producers, including winding and wheeling ma-
- terial B—Pumping vitriol over Gay Lussac and Glover towers
- B-Working iron oxide briquette plant
- A-General laboring
- A-Genera
- TUNGSTEN
  - A-Crushing, sieving, and packing
- WASTE ACIDS
- BD-Operating denitration plant, all operations
- ZINC DISTILLATION B-Making fireclay moulds and condensers

## TWO LETTERS ON EFFECT OF COAL ASH ON THE NATURE OF CEMENT MILL POTASH

#### Editor of the Journal of Industrial and Engineering Chemistry:

In a recent article by Messrs. Potter and Cheesman,<sup>1</sup> attention has been called to the fact that in some cases the coal used as fuel for the burning of cement carries sufficient potash to affect both the total amount of potash driven from the kiln and the nature or condition of the potash occurring in the resulting flue dust. The statement is made that the so-called "recombined potash," which has previously been assumed to be the result of a combination of the potash vapor and the floating coal-ash particles,<sup>2</sup> is only that potash held in the ash and originally contained in the coal, together with the undecomposed and insoluble potash contained in the dust or raw mix mechanically blown out of the kiln.

Investigations conducted in this laboratory by the writers, and at the factory of the Security Cement and Lime Company, in coöperation with Mr. Haff, chief chemist for that company, have led to conclusions which are at variance with those above set forth. As these questions may in some instances become very important in the future the following data are submitted so that they may form a part of the printed literature available to the cement mill chemist and engineer.

Coals from nine different cement plants, both in this and foreign countries, have been analyzed at this laboratory for ash and potash, with the following results:

No. of Plant	Location	Ash in Coal Per cent	K2O in Ash Per cent	K2O in Coal Per cent
1 3 4 6 8	Ohio Maryland Michigan Michigan Michigan Michigan South America	$ \begin{array}{r} 10.45 \\ 9.23 \\ 10.60 \\ 14.55 \\ 10.38 \\ 17.75 \\ 12.07 \\ 19.65 \\ \end{array} $	$\begin{array}{c} 0.66\\ 1.43\\ 1.96\\ 1.90\\ 2.08\\ 4.64\\ 1.73\\ 0.71 \end{array}$	$\begin{array}{c} 0.069\\ 0.132\\ 0.208\\ 0.276\\ 0.216\\ 0.824\\ 0.209\\ 0.140\\ \end{array}$
9 Average	New Zealand	$\frac{11.02}{12.85}$	$\frac{0.89}{1.77}$	$\frac{0.098}{0.241}$

It will be noted that the highest potash content of the coals, represented by these nine samples, is equivalent to 0.82 per cent  $K_2O$ , while the average is equivalent to only 0.241 per cent  $K_2O$ . Ignoring the abnormally high potash sample marked No. 6, the average of the eight remaining samples becomes only 0.1687 per cent  $K_2O$ . On the other hand, the potash content of the resulting ash of the full nine samples is equivalent only to 1.77 per cent  $K_2O$ , and should we ignore sample No. 6, the average potash content of the ash becomes only 1.42 per cent  $K_2O$ . From this it would appear that the samples investigated by Messrs. Potter and Cheesman have an abnormally high potash content, particularly as determined by analysis of the ash.

The amount of coal consumed per barrel of cement burned varies greatly in the different mills throughout the country, and it is very difficult to strike an average. As indicated in Messrs. Potter and Cheesman's article, the coal consumption varies possibly from 80 lbs. per barrel to 250 lbs. per barrel, as the extreme limits. The average coal consumption for the plants from which the above nine samples were taken is 135 lbs. of coal per barrel of clinker produced. This figure also holds approximately for the remaining eight samples, should we ignore the high potash Sample No. o. Using these eight samples as the basis for calculation, we find that there is introduced into the kiln with the coal, an amount of potash equivalent to 0.23 lb. of K2O for every barrel of clinker produced. Since the average potash content of the cement raw material used in these eight plants is approximately 0.75 per cent K2O, there is introduced into the kiln with the raw material, an amount of potash equivalent to 4.5 lbs. K2O for every barrel of clinker produced. It would seem from this that the potash introduced with the coal

<sup>1</sup> THIS JOURNAL, 10 (1918), 109.

2 Ibid., 9 (1917), 646.

is approximately only 5 per cent of the total potash entering the kiln.

Meade, in his book on Portland cement, states that probably half of the ash from the coal drops in the kiln, and is then carried out with the clinker. It is difficult to determine, with accuracy, the amount of coal ash that actually is carried out with the clinker, or that which is blown out with the gases. Messrs. Potter and Cheesman assume that only 25 per cent of the coal ash is carried out with the clinker, even in a wet kiln, which is probably a very low figure. However, should we assume this minimum figure, as used by Potter and Cheesman, and also assume only a 40 per cent volatilization of the potash carried by the raw material, it follows that even then less than 10 per cent of the total potash carried out with the gases can possibly come from the coal. It is evident, therefore, that the coal ash is of relatively minor importance, so far as the total potash blown from the kiln is concerned. The relatively small amount of potash introduced with the coal also makes it improbable that this can effect any material change in the nature or condition of the total potash material collected.

The authors referred to, state in their article "that taking into consideration the K2O content of the ash, and the K2O in the raw mix carried over mechanically, there is apparently no recombination of the volatilized K2O with siliceous ash particles." In connection herewith, the following figures taken from a factory where potash is actually being collected commercially, may be of interest, particularly as these figures are representative of the nature of the material collected over a period of several months. During the period of operation represented by the samples, the coal burned in the kilns had a potash content equivalent to 0.132 per cent K2O. Approximately 80 lbs. of this coal were burned per barrel of clinker produced. There was thus introduced into the kiln with the coal, an amount of potash equivalent to 0.11 lb. K2O per barrel of cement burned, while about 6 lbs. of K2O per barrel were introduced with the raw material. During this period the dust collected from the stack gases carried, as insoluble and slowly soluble potash, an amount of potash equivalent to 0.88 lb. K2O per barrel of clinker produced in the kilns. The terms "insoluble" and "slowly soluble" are used here in the sense that the so-called insoluble portion is not affected by long boiling, and is only appreciably soluble in weak hydrochloric acid, while the so-called slowly soluble portion is completely dissolved by either method, both insoluble and slowly soluble being differentiated, however, from the soluble potash, which dissolves readily in hot water. Of this total of 0.88 lb. of insoluble and slowly soluble potash, approximately 0.30 lb. was in the insoluble form, and 0.58 lb. in the slowly soluble form.

The insoluble potash, equivalent to approximately 0.30 lb. of  $K_2O$  per barrel, can be accounted for on the assumption that it represents the potash in the dust or raw mix mechanically blown out of the kiln. The total amount of dust recovered during this period, per barrel of clinker produced, is equal to approximately 20 lbs. The analysis of this dust indicated it was 50 per cent calcined, which would give a potash content of this dust of approximately 1.4, on the assumption that none of its potash had been volatilized. This latter assumption can unquestionably be made, as none of this dust had at any time been subjected to a high temperature. This dust should, therefore, contain 0.28 lb. of  $K_2O$  in insoluble form, which figure checks fairly accurately with the insoluble potash determined by analysis.

This indicates that the slowly soluble potash present in an amount equivalent to 0.58 lb. K<sub>2</sub>O per barrel of cement burned, must have come from sources other than the dust mechanically blown out of the kiln. Should we make the improbable and extreme assumption that all of the coal ash was carried out with the gases, and that none settled in the kiln to be carried

out with the clinker, this would still account for an amount of potash equivalent to only 0.11 lb. K2O, as arising directly from the coal ash. This extreme assumption that the total coal ash is carried out of the kiln, therefore, still makes it necessary for us to account for 0.47 lb. K2O per barrel of clinker produced. It follows then that this must have come from sources other than the dust blown out of the kiln or the coal ash carried out with the gases. The only other source from which potash could have been derived is the potash vapor resulting from the volatilization of the potash from the kiln burden. The assumption that the incandescent siliceous coal-ash particles react with this potash vapor is not an unreasonable one, and from the information at hand it appears that this is the explanation of the cause or source of the greater part of the "slowly soluble" potash occurring in the collected dust, as outlined in the former paper above referred to.

Moreover, as was pointed out in that paper, such an explanation is not new. Thus, Henry S. Spackman, in a patent dated October 24, 1916, states that it is well known that the considerable portion of the alkali in the collected dust from cement kilns that is insoluble is due to the union of the volatilized alkali with highly heated, finely divided, siliceous dust to form glass.

From analyses made of dusts from several other cement factories it appears that the figures given above for the plant in question do not represent abnormal conditions, for some flue dusts have even a much larger amount of "slowly soluble" potash as compared with the amount of potash carried into the kiln with the coal.

Considering further that for every barrel of cement burned there is introduced into the kiln with the raw material an amount of potash equivalent to 6.00 lbs. of  $K_2O$ , while only 0.11 lb. of  $K_2O$  are added with the coal, it will be readily seen that the potash introduced with the coal has a relatively small bearing upon the question of by-product potash manufactured in rotary kilns, where only the soluble potash comes into consideration. In making accurate potash calculations, however, where the total "potash" is of interest, the potash introduced with the coal and carried by the coal ash should be carefully considered, as pointed out by Messrs. Potter and Cheesman.

#### SUMMARY

I—The coal used in cement burning carries comparatively small amounts of potash, the average being only 0.24 per cent  $K_{2}O$  for the nine plants investigated.

II—The amount of coal-ash potash introduced into the kiln is ordinarily very small as compared with the amount of potash entering the kiln with the raw material.

III—The sum of the insoluble and slowly soluble potash collected from coal-burning kilns, exceeds the sum of the total potash contained in the coal and in the raw material mechanically blown from the kiln.

	L. ANDERSON
LABORATORIES OF THE	R. J. NESTELL
WESTERN PRECIPITATION COMPANY	in J. Hubidad
LOS ANGELES, CALIFORNIA, April 15, 1918	

#### Editor of the Journal of Industrial and Engineering Chemistry:

In February 1918, there appeared in THIS JOURNAL, page 109, an article by N. S. Potter, Jr., and R. D. Cheesman, entitled "Effect of Coal Ash on the Liberation and Nature of Cement Mill Potash." In this paper, the authors make the following statement: "The potash collected from the kiln stack gases where coal is used for burning appears in practically two forms, water-soluble potash and the insoluble or slowly soluble potash. The insoluble potash has been attributed to two causes: the potash in the unburned or partly calcined raw material carried over mechanically in the gases and to a recombination of the volatilized potash with the finely divided ash particles of the coal." Potter and Cheesman refer to an article<sup>1</sup> in which appears this statement: "In some plants where coal is used for burning, the extent to which the potash occurs in the 'recombined' form may be considerable, while in certain other plants where oil is used for fuel this combination of the potash is present in comparatively small amount." From this statement they deduce, "It is evident that the potash content of the coal ash has been quite neglected."

From the experimental data which are recorded in this article, Potter and Cheesman arrive at the following conclusions:

"I-K<sub>2</sub>O content of coal ash is considerable.

 $''II-K_2O$  content of coal ash must not be disregarded in calculating the liberation in kilns.

"III—K<sub>2</sub>O content of coal ash appears in 'treater dust' as insoluble  $K_2O$ .

"IV—Taking into consideration the  $K_2O$  content of ash and the  $K_2O$  in raw mix carried over mechanically there is apparently no 'recombination' of the volatilized  $K_2O$  with the siliceous ash particles."

The above deductions do not agree entirely with observations that have been made and experimental data that have been collected at the plant of the Security Cement and Lime Company, Hagerstown, Md. Therefore, these observations and data are discussed in connection with the conclusions derived by Potter and Cheesman.

"I— $K_2O$  content of coal ash is considerable," In support of this contention Potter and Cheesman analyzed four samples of coal ash (each representing the average for one week) and found that "the average potash content figures close to 5 per cent" from which they conclude that the amount of potash introduced by the coal per barrel of clinker produced lies between 0.4 lb. and 1.25 lbs., depending upon the type of plant. In Table I are given the results obtained by the analysis of six samples of Fairmont gas coal used by the Security Cement and Lime Company.

TAE	BLE I	
Average Sample for 24 hours ending	Ash in Coal Per cent	K2O in Ash Per cent
10-29-17 10-30-17 10-31-17 11-1-17 11-2-17 11-3-17	8.85 9.00 9.25 9.25	$     1.77 \\     1.68 \\     1.23 \\     1.95 \\     1.84 \\     1.65   $
Average		1.68

Numerous determinations of the  $K_2O$  in coal ash have been made at the laboratory of the Security Cement and Lime Company since the above table was prepared, and in no case did the result exceed 2 per cent.

If the coal consumption at different plants ranges from 80 to 250 lbs. per barrel of clinker, the average of the results given above would show the possibility of the introduction of only 0.12 to 0.37 lb. of  $K_2O$  per barrel of clinker as contrasted with 0.4 to 1.25 lbs., according to the calculations of Potter and Cheesman.

The following data were secured from information furnished by the Bureau of Mines.

TABLE II-ALKALIES IN ASH OF WEST VIRGINIA COALS

County	Town	K <sub>2</sub> O in Coal Ash Per cent
Barbour	. Century	1.91
Fayette		1.92
Fayette		1.33
Fayette		
McDowell		0.69
McDowell		0.34
McDowell		0.82
Mercer		1.89
Mercer		2.09
Monongahela		1.00

Table III, in which are given the per cent ash and per cent  $K_2O$  in ash for ten samples of Fairmont gas coal as they are presented on pages 334 and 335, Bulletin 2, West Virginia Geological Survey, 1911, is also of interest in this connection.

<sup>1</sup> W. H. Ross and A. R. Merz, "The Recovery of Water-Soluble Potash as a By-Product in the Cement Industry," THIS JOURNAL, 9 (1917), 1035.

	TABLE III		
Sample No.		Ash er cent	K <sub>2</sub> O in Ash Per cent
1		5.72	1.23
3		7.42	0.92
4		6.42	1.03
6 7		6.04 8.14	0.89 0.75
8		7.22 7.11	0.84 0.96
10		7.50	0.95
AVERAGE		6.94	0.94

The figures presented in Tables II and III substantiate the results of the analyses made at the laboratory of the Security Cement and Lime Company.

" $II-K_2O$  content of coal ash must not be disregarded in calculating the liberation in kilns." By percentage liberation is meant the per cent of  $K_2O$  contained in the raw material which is volatilized in the kiln during the process of burning. At the plant of the Security Cement and Lime Company it is calculated as follows:

#### Percentage liberation =

It is considered that 580 lbs. of raw material must be actually burned in the kiln to make 380 lbs. of clinker.

Potter and Cheesman assume that in a dry process plant 90 per cent of the coal ash passes up the flue with the gases. If, in addition to this, we were to assume that (1) 90 lbs. of coal are burned per barrel of clinker, (2) the coal contains 10 per cent ash, and (3) the potash content of the ash is 2 per cent, then the amount of  $K_2O$  deposited in the kiln by the ash would be 0.018 lb. per barrel of clinker, or 0.0047 per cent of the weight of the clinker. If it were found by analysis that the raw material contained 1.2 per cent  $K_2O$  and the resulting clinker 0.60 per cent, as ordinarily calculated, the percentage liberation would be

$$\frac{580 \times 1.2 - 380 \times 0.6}{580 \times 1.2}$$
, or 67.2 per cent.

If from the per cent  $K_2O$  determined to be present in the clinker 0.0047 per cent be subtracted (assuming that all of the potash deposited by the coal ash in the kiln emerged with the clinker), the percentage liberation would become

$$\frac{580 \times 1.2 - 380 \times 0.5953}{580 \times 1.2}$$
, or 67.5 per cent.

Even though the  $K_2O$  content of the coal ash were 5 per cent, the percentage liberation would be only 67.7. Therefore it would seem that the effect on percentage liberation of the  $K_2O$ in the coal ash, in dry process plants at least, is negligible.

"III— $K_2O$  content of coal ash appears in 'treater dust' as insoluble  $K_2O$ ." At this point, attention is directed to the fact that instead of two there are in reality three forms of potash present in treater dust.<sup>1</sup> They are designated as water-soluble, acid-soluble or slowly water-soluble, and acid-insoluble. In speaking of insoluble potash, a distinction should be made between that which is acid-insoluble and that which is often referred to as insoluble in water, for the latter includes both the acid-soluble or slowly water-soluble and acid-insoluble portions. It is evident that Conclusion III refers to water-insoluble potash, since in an earlier portion of their paper Potter and Cheesman state, "the potash collected from the kiln stack gases where coal is used for burning appears in practically two forms, watersoluble potash and the insoluble or slowly soluble potash."

"IV—Taking into consideration the  $K_2O$  content of ash and the  $K_2O$  in raw mix carried over mechanically there is apparently no 'recombination' of the volatilized  $K_2O$  with the siliceous ash particles." In order to determine the accuracy of this statement, several tests were conducted at the plant

1 W. H. Ross and A. R. Merz, THIS JOURNAL, 9 (1917), 1035.

of the Security Cement and Lime Company, using a kiln and treater that comprise one of the units of the plant. In each case the duration of the test was 24 hours. Necessary precautions were taken to determine as accurately as possible the weights of clinker, stack-, base-, and treater-dust produced, and to obtain an average sample of each. A sample of coal representing the average for the entire period of each test was secured by an automatic coal sampler.

In Table IV are given the data that were obtained from the analysis of the various samples collected in three of the tests; in Table V are the results of calculations based on the data in Table IV.

TABLE IV			
Test number	1	2	3
Barrels of clinker made	498.73	553.94	551.53
Coal:	State State		
Tons used	22.44	24.93	24.81
Per cent ash	6.95	7.77	8.97
Per cent K2O in ash	0.42	1.51	1.38
Treater dust:			Sale Parts
Tons drawn	6.75	7.75	6.8
Per cent water-soluble K2O	8.82	10.18	8.42
Per cent acid-soluble K2O	1.80	0.64	1.30
Per cent acid-insoluble K2O	0.48	0.84	1.38
Per cent total K2O	11.10	11.66	11.10
Stack-base dust: Tons drawn	0.15	2 20	0.00
	2.15	3.30	0.90
Per cent water-soluble K20 Per cent acid-soluble K20	3.06	4.58	3.53
Per cent acid-insoluble K <sub>2</sub> O	1.09 0.43	1.17	1.36
Per cent total $K_2O$	4.58	4.97	0.43 5.32
rer cent total Rio	4.30	4.97	3.32
TABLE V-POUNDS K2O PER BARI	REL OF C	LINKER	
Test number	1	2	3
In treater dust + stack-base dust:		ANE THE	
Water-soluble	2.651	3.275	2.192
Acid-soluble	0.58	0.318	0.365
Acid-insoluble	0.16	0.261	0.354
Total	3.399		2.911
In coal ash entering kilns	0.020	5 0.105	0.111

According to Potter and Cheesman, the  $K_2O$  content of the coal ash and the  $K_2O$  in the raw mix carried over mechanically should account for all the water-insoluble potash collected. In this connection the figures presented in Table VI are of interest.

TABLE VI-POUNDS K2O COLLECTER	PER B	ARREL	OF CLIN	KER
Test number	1	2	3	4
Water-soluble potash (K2O)	2.651	3.275	2.192	2.706
Water-insoluble potash:				
Acid-insoluble (raw mix blown over)	0.167	0.261	0.354	0.260
Acid-soluble (slowly water-soluble):				
Coal ash blown over (90 per cent)	0.023	0.094	0.099	0.072
Partially burned material	0.558	0.224	0.266	0.349
Recombined				
Total K20	3.399	3.854	2.911	3.387

It will be observed that, after deducting from the total K<sub>2</sub>O<sup>4</sup> the water-soluble potash and the sum of the potash content of the raw mix and of the coal ash carried over by the flue gases, there still remains a portion, the average of which for the threetests amounts to 0.349 lb. per barrel of clinker, or 10.31 per cent of the total potash collected. Moreover, the sum of the potash content of the raw mix carried over mechanically and of the coal ash blown over (which amounts to 0.332 lb. per barrel of clinker) is sufficient to account for only one-half of the waterinsoluble portion. As indicated in Table VI, the other half may not all be recombined potash; it is reasonable to suppose that it may be made up, in part at least, of raw material that has been only partially burned, thus making the potash compounds which it contains acid- or slowly water-soluble. That such partial decomposition does take place is clearly shown by an analysis, given in Table VII, of a sample of treater dust obtained by W. H. Ross and A. R. Merz1 from the plant of the-Riverside Portland Cement Company.

TABLE VII

COMBINATION	KtO in Treater Dust Per cent	Total K2O in Dust Per cent
• Water-soluble Slowly soluble Acid-insoluble	0.7	91.59 6.54 1.87
Total	10.7	100.00

<sup>1</sup> W. H. Ross and A. R. Merz, U. S. Dept. Agriculture, Bull. 572 (1917), 10.

At the Riverside plant, oil is used as fuel. Since in such a plant no coal ash is present with which the volatilized potash may recombine, the small amount of slowly-soluble potash that is found in the treater dust must be due either to partially burned material or to a recombination of some of the volatilized potash with siliceous material in the raw mix.

At the plant of the Security Cement and Lime Company (where powdered coal is used for fuel) it is now customary to add a small proportion of sodium chloride to the raw mix for the purpose of decreasing recombination. A patent covering this process has been applied for by R. C. Haff, Chief Chemist, and R. D. Cheesman, formerly assistant chief chemist of the Security Cement and Lime Company. Pefore this practice was started, the treater dust produced contained a high percentage of water-insoluble potash, and yet at that time the operation of the kilns was practically the same as at present, approximately the same quantity of coal was consumed per barrel of clinker, and probably about the same quantities of raw and partially burned materials were carried out of the kilns. Therefore the sum of the quantities of K<sub>2</sub>O in the coal ash and in the raw and partially burned material carried over in the kiln gases must have been approximately the same as now, but the amount of recombined potash was considerably higher and the watersoluble portion correspondingly lower.

In Table VIII are given the analyses of two samples of Security treater dust. The first was obtained by Ross and Merz before the practice of adding sodium chloride to the raw mix was started; the second is the sample from Test No. 1, the data for which are given in Tables IV, V, and VI. These particular samples were chosen because they are almost identical in their respective percentages of total and acid-insoluble potash, therefore making it possible to compare accurately the percentages of recombined and water-soluble potash which they contain.

TABLE VI	II	
		After Addition of Sodium Chloride
Water-soluble <sup>T</sup> K <sub>2</sub> O, per cent Acid-soluble K <sub>2</sub> O, per cent Acid-insoluble K <sub>2</sub> O, per cent	6.80 4.10 0.50	8.82 1.80 0.48
Total K2O, per cent	11.40	11.10

It will be noted that (1) the potash content of the treater dust due to raw material carried over by the flue gases (indicated by the amount of acid-insoluble  $K_2O$  determined) is approximately the same in each case, (2) there has been a decrease of approximately 2.3 per cent in the amount of acid-soluble potash, with a corresponding increase in the amount of water-soluble  $K_2O$ .

Assuming that the amount of partially burned material carried over with the flue gases is approximately the same at the Security and Riverside plants, and that this amount of the Riverside plant as shown in Table VII is approximately 6.54 per cent of the total potash recovered, the percentages of this material present in the treater dust must have been about 0.74 before and 0.73 after the addition of salt to the raw mix. Subtracting these amounts from the percentages of slowly-soluble K2O given in Table VIII, the recombined K2O present in the treater dust collected at the Security plant must have been approximately 3.37 per cent before and 1.07 per cent after the addition of sodium chloride, showing a reduction in recombination of approximately 2.3 per cent of the weight of the dust or 20.3 per cent of the total potash collected. In other words, by the introduction of sodium chloride vapors into the zone of combustion, thereby causing the preferential formation of potassium compounds which answer the official requirements as to "soluble potash," the Security Cement and Lime Company has decreased recombination approximately 68.0 per cent and at the same time has obtained an increase of 32 per cent in the percentage of water-soluble K2O present in the treater dust which amounts to 20.3 per cent of the total potash collected.

#### SUMMARY

Results obtained at the Security Cement and Lime Company do not substantiate the conclusions regarding potash liberation reached by Potter and Cheesman.

The effect on potash liberation as here calculated is not greatly influenced by the low percentages of  $K_2O$  present in the coals used.

When salt is added to raw mix the percentage of water-soluble  $K_2O$  in the treater dust increases at the expense of acid-soluble  $K_2O$ .

This is explained satisfactorily only on the assumption that recombination to the extent of about 68 per cent has been prevented.

Grateful acknowledgment is made to Mr. H. S. Bair who assisted in the experimental work, and to C. H. Miller, H. C. Mackenzie, and J. E. Baker who made the analyses reported, under the direction of Mr. R. C. Haff.

E. O. RHODES AND J. J. PORTER

THE MELLON INSTITUTE OF INDUSTRIAL RESEARCH UNIVERSITY OF PITTSBURGH, PA.

The Security Cement and Lime Company Hagerstown, Md. May 1, 1918

## WASHINGTON LETTER

#### By PAUL WOOTON, Union Trust Building, Washington, D. C.

So unexpected was the collapse" of the enemy, just at a time when the Government's war machine was most intent on quantity production, that the armistice caught the authorities without a reconstruction policy. In fact, there was not a single definite plan for the conversion of the war machine to a peace basis.

Strenuous efforts are in progress to evolve definite reconstruction policies but nothing comprehensive has come out during the week following the signature of the armistice. Individual ideas, however, are beginning to become available which indicate the general trend of thought. The most important single development is that there is to be no wholesale cancelling of contracts. The curtailment is to be allocated in much the same manner as that in which the contracts were let. This work is to be engineered by the War Industries Board with special coöperating agencies within the departments interested. Due recognition is being taken of the labor situation, both in the curtailing of contracts for raw materials and in the mustering out of the Army. Before cancelling or reducing any contract, reports must be made to the War Industries Board showing the following: (a) The effect of the proposed cancellation on the industry.

(b) The effect on labor conditions.

(c) The effect on the given locality.

(d) The effect on the given contractor.

By far the most comprehensive statement as to the industrial aspects of the reconstruction period has been made by Benedict Crowell, director of munitions for the War Department, as follows:

With the signing of the armistice, the War Department is faced with an intricate problem and great responsibilities. The industries of the country, which have responded whole-heartedly to the call of the Government for increased production and which were going at a rate never before attained, must be diverted from war-time production to their normal occupations in times of peace.

The first and primary consideration in getting back to this normal basis is to make this readjustment with as little inconvenience as possible, and with a continuous employment of labor.

It is also essential that the production of material for war, which means now a waste of material which could be used for civilian population both here and for the purposes of reconstruction in Europe, should be stopped as speedily as is consistent with the primary consideration of labor and the industries.

Instructions have therefore been issued to all Bureaus of the War Department, governing the methods of slowing down of production, so that as far as possible there should be a tapering off of war work, giving time for industrial readjustment and for the industry to take up civilian work.

So that manufacturers might as rapidly as possible get into work on civilian needs, at our request the War Industries Board have withdrawn all priority ratings on army work.

No order is being suspended or cancelled by the War Department without consideration of the nature of the work or the locality in which the work is being performed, labor, and the re-employment of labor at such places in other industries, and without conference and consultation with the War Industries Board which has been constantly in touch with the industries of this country, and with the Department of Labor, which is in intimate touch with the conditions of employment in all parts of the United States.

Overtime, holiday, and Sunday work has been stopped, and as rapidly as possible and as rapidly as the labor can be used in normal day shifts, night shifts will be discontinued.

It is often the case that in a certain locality where labor is working on a war project, this work may be stopped and the same labor utilized on other work in the same locality.

During the war, production has been largely diverted from articles called for in times of peace to war necessities, and civilian needs have been curtailed and non-essentials largely eliminated. With the assistance of the War Industries Board the articles for war necessities are being rapidly curtailed and the industries proportionally freed to work on civilian needs. Industries which have been largely concentrated in certain areas with resultant congestion of transportation, with a great influx of labor in this area, with inadequate facilities for housing, etc., are being taken into consideration in this readjustment.

The two standards which the War Department has set up for itself are that these contract readjustments must be made equitably, in regard to the industry and labor, and promptly, to safeguard the financial elements of the problem.

Of no small interest to the chemical industries is the matter of the future of the large number of women now engaged. Miss Mary Van Kleeck, the director of the Women in Industry Service of the Department of Labor, expresses the following thoughts in this connection:

The question peculiar to women relates to those who have taken men's places. It would seem fair to the returning soldiers that they be reinstated in their old positions, but in justice to the women who have taken their places, sufficient notice should be given to enable them to be transferred to other work. The number of women who have been drawn into gainful employment for patriotic reasons is probably much smaller than is generally supposed. Large numbers of women in the war industries have been transferred from other occupations and the problem of readjustment is to return these workers to their normal occupations.

With the need for production to feed and clothe and shelter other nations besides our own there is no reason to believe that the employment of women in industry will not increase rather than decrease. In view of the responsibility of women for their own support and often for the support of dependents they cannot be asked to withdraw entirely from gainful employment.

That there is an important demand for the continuation of government control in many industries is indicated by the agreements which have been reached at a meeting of the War Industries Board and the copper industry and of the War Industries Board and the steel industry. The copper-producing industry, represented by Daniel Guggenheim, C. F. Kelley, Daniel C. Jackling, and R. L. Aggassiz, made a hard-and-fast agreement with the War Industries Board, in which the principal points are:

(a) The present rate of production is to be maintained in the mines, smelters, and refineries, continuous employment being thus insured during the first period of the transition from a war to a peace basis.

(b) The present level of prices of the metal and the existing wage scale of labor are to be preserved.

(c) The War Industries Board, or such other governmental agency as may be designated, is to continue regulation of prices and allocation of the material.

The agreement is subject to renewal or revision January 1.

Following the meeting, Bernard M. Baruch, the chairman of the War Industries Board, commented significantly on the copper situation. Practically the same situation exists with regard to many chemical products. The remarks of Mr. Baruch are substantially as follows:

One of the allied governments within the last twenty-four hours has requested information on delivery of 200,000 tons of copper. This is accepted as a sign that the European demand will not only be large but immediate. Prospective requirements for civilian consumption, due to the curtailment of the productivity of many American industries for the last eighteen months because of the needs of the war program, have created a demand that is expected to prove a factor in stabilizing conditions generally.

The civilian demands in Europe and elsewhere, held in check for more than four years, will work to the same end.

The demand for copper will be heavy, and most of it must be met by the United States, as between 75 and 85 per cent of the copper production is in the hands of American industry. With the refining facilities included it is probable that the proportions controlled by American producers is nearly 90 per cent.

After the conference with the heads of the steel industry, the War Industries Board made a formal announcement of which the following is a paragraph:

The Iron and Steel Institute Committee, in the course of its suggestions, placed emphasis upon the point that a continuation of governmental supervision of industry for the present was highly desirable. It was agreed that many changes in operating conditions of the steel mills will be necessary in the transition from a war to a peace basis. Some cancellations and adjustments in war contracts will follow, but owing to the removal of many restrictions imposed on non-war industries and the immediate demands of such industries and a probable resumption of Federal, State, and Municipal improvements which had been temporarily suspended, and the demands from abroad for foreign construction which are already taking definite shape, it is believed that the transition can be accomplished in an orderly and systematic way.

An announcement from the President with regard to use which will be made of the powers conferred upon him by the War Minerals Act is expected soon. He already has authorized the use of \$100,000 of the appropriation carried by the Act, for the stimulation of the production of potash, arsenic, and zirconium. This work already is under headway. It is being directed by J. E. Spurr, in charge of the War Minerals Section of the Bureau of Mines.

In addition, however, it has been suggested to the President that a comprehensive effort be made looking to the development of the potash industry to the point where the United States will be independent of outside sources. It is contended that the War Minerals Act gives a rare opportunity to get this industry on its feet. Many are of the opinion that the German product can be undersold in addition to reducing the price of cement and pig iron, which would be possible when the potash byproduct is recovered.

The Department of Agriculture is interested equally with the Bureau of Mines in the development of a domestic potash industry. Wallace W. Mein, the assistant secretary of agriculture, is giving the matter a considerable portion of his personal attention. Potash hunger has manifested itself in crops from Maine to Florida. This demonstrates, he believes, that potash is a necessary ingredient of fertilizers. He regards as very dangerous the propaganda which has been conducted by certain fertilizer interests to the effect that potash is not necessary to proper fertilization of soil. On the other hand, he regards it as essential to discount the preaching of the German potash industry which urged the use of excessive amounts of potash and fertilizer. By finding the middle ground between these extremes, the best interests of American agriculture will be met, Mr. Mein says. He deprecates the policy which has allowed large quantities of domestic potash to go unused during the war.

Disbanding of the Chemical Warfare Service of the Army began with the signing of the armistice. Whether the skeleton of the organization will be retained is a matter of question. Some contend that chemical warfare is a development of the times and may be retained. Such a view is strengthened by reference to the loud protest which went up when the British army first made use of shrapnel. It was characterized as inhuman and barbaric. Any continuance of the use of gas in warfare is condemned by the men who directed the service in the American army. Should the international situation not be adjusted stably, and should nations continue to compete in armament, it is admitted that the Chemical Warfare Service probably would become a permanent branch of the Army. As no such outcome is anticipated, present preparations are being made largely on a basis of complete disbanding.

At the date of this writing the entire staff of the Chemical Warfare Service is continuing with the work. Maj. S. W. Avery is an exception. His resignation was given preference that he might return to especially urgent work at the University of Nebraska. Many other resignations, however, have been submitted and prompt action on them is expected. The personnel of the service is being released in compliance with the War Department's general policy of not returning men from the Army faster than they can be absorbed in the industries. This does not affect chemists as importantly as men in other industries. Most of the chemists who have been working with the Chemical Warfare Service have positions awaiting them. There is to be no uncertainty in this particular, however, as Major Allen Rogers, the chief of the Industrial Relations Branch of the Chemical Warfare Service, has sent to each man a series of questions which will establish his status with regard to his employment in civil life.

Major Rogers is of the opinion that the demand for chemists will be very much greater as a result of the many practical demonstrations during the war of their worth in many industries. The presence of Army chemists in so many plants has taught manufacturers many lessons in the handling of their business.

The manufacture of toxic substances already has been stopped. This portion of the chemical service had attained large proportions with the end of the war. The manufacturing capacity of the United States of these substances was greater at that time than those of England and France combined. Large supplies of materials entering into gases are on hand. As they cannot be stored for any great length of time, their disposition is offering a problem.

It is not claimed at the offices of the Chemical Warfare Service that gases superior to those in use by the Germans were produced. That the best German efforts were equalled is a claim which it is practically certain will be established. In the development of the gas mask, however, there is no question that the best efforts of the enemy or of the Allies were outdone. Important announcements along these lines may be expected after the conclusion of peace.

Over 13,000 replies have been received to the questionnaire which was sent to chemists in September by the Chemical Warfare Service. The number of questionnaires originally sent was 18,000. Classification of the replies received has been completed. There are more than 100 classes into which the chemists are separated.

Chemists in Washington expect to see material improvement when the chemical departments of schools and colleges are reorganized. The war has resulted in the disorganization, it is said, of the chemical departments at most of the institutions for higher education. The remarkable advance made by the chemical industries during the war, as well as the practical experience which has been attained by so many of the chemical instructors and pupils will result in a very material improvement, it is believed.

In this connection it may be stated that a frequent criticism heard in Washington of the Chemical Warfare Service, is that the college professors had too much to say regarding its management. Their inability in certain cases to apply practical methods is said to have delayed the program to some extent. Had industrial chemists had a greater voice, some believe progress would have been more rapid. At any rate, all admit that those connected with the Service have had some very valuable practical training.

At the close of hostilities there were 1500 chemists on active duty with the Chemical Warfare Service. This is in addition to 3000 other men with chemical training, who also were on active duty.

With reference to America's war system of economic control, Chairman Baruch, of the War Industries Board, has called attention to an editorial published in the *Frankfurter Zeitung*, not long before Germany laid down her arms, lamenting the fact that Germany had not adopted the far-sighted methods of the United States to check abnormal rises in the prices for raw materials needed in the war program. Opposed at first to the price-fixing regulations of the Government, observed Mr. Baruch, the industrial leaders of America have themselves come around to appreciate the wisdom of the President in insisting upon a check on the prices for the basic materials where scarcity stimulated the tendency towards extraordinarily high levels. Had a different policy been pursued, said Mr. Baruch, the steel and iron industry, for example, would be facing a return to peace conditions with the price for pig iron boosted up to \$150 a ton or more, and other items of their production similarly scaled. It is in appreciation of the value of a restraining influence, he said, that the steel industry and others are asking that government control be extended over the period of transition from a war to a peace basis.

## PERSONAL NOTES

First Lieutenant Elbert C. Baker, son of Mr. and Mrs. J. T. Baker, of Easton, Pa., was killed in action in France on September 30. Lieutenant Baker graduated from Cornell Univ versity in 1915 and then took an extra year of special work in chemistry, receiving the degree of Bachelor of Chemistry. After leaving Cornell he was associated with his father at the J. T. Baker Chemical Works in Phillipsburg, N. J.

Professor William Main, scientist and engineer, and formerly professor of chemistry in the University of South Carolina, died recently at his home in Piermont, N. Y. Professor Main was one of the pioneers of the copper and lead mining industries of this country. He was the inventor of the lead-zinc storage battery, and the first to apply the storage battery to the propulsion of street cars.

Mr. William E. Garrigue, a member of the Chicago Section of the American Chemical Society and for many years prominently identified with the chemical industry of this country, died at Toronto, Canada, on October 2, 1918.

Mr. H. M. Barkesdale, vice president of E. I. du Pont de Nemours & Co., Inc., died of influenza at Wilmington, Del., on October 18, 1918.

Mr. Roy O. Fitch, of the Bureau of Standards, died on October 13, 1918. His work with the Bureau of Standards was chiefly on bituminous materials of construction.

Mr. Thomas Bartlett Ford, associate physicist of the Bureau of Standards, died on October 1, 1918. He had been for several years in charge of the low-temperature laboratory of the Bureau, including the liquid air and liquid hydrogen apparatus and had devoted considerable attention to the separation of rare gases.

Mr. Milton Birch, vice-president and treasurer of the Westmoreland Chemical and Color Company died in October after a brief illness. Miss Elizabeth S. Weirick, for the past eight years instructor in chemistry at Pratt Institute, Brooklyn, N. Y., has resigned her position there to take up the work, on January I, of textile chemist in the chemical laboratories of Sears Roebuck and Company, Chicago.

At the request of the Board of Regents of the University of Nebraska, the War Department has permitted Major Samuel Avery, chief of the University Relations Branch, Chemical Warfare Service, to resign his commission, in order to resume his duties as Chancellor of the University, on December I. Major Victor Lenher, in addition to his other duties in the Relations Section, now takes charge of the work relinquished by Major Avery.

At the meeting of the New York Section of the Société de Chimie Industrielle on November 19, addresses were made by George Maoussa, Docteur des Sciences, Member of the French High Commission, and C. O. Mailloux, E.E., M.S., D.Sc., Past President of the American Institute of Electrical Engineers, Member of the American Industrial Committee to France.

Dr. W. M. Burton was recently elected president of the Standard Oil Co. of Indiana, to succeed the late Lauren J. Drake. Dr. Burton has been connected with the company for many years, having been chief chemist, superintendent, general manager, and vice president.

Mr. G. D. Cain, chief chemist of the fertilizer control laboratory at the Louisiana Agricultural Station, has been appointed assistant director of the North Louisiana Station at Calhoun.

Mr. J. S. Jones has resigned as director and chemist of the Idaho Agricultural Experiment Station and professor of agricultural chemistry in the University of Idaho, and has assumed charge of the laboratory of one of the government nitrate plants under the Ordnance Division of the War Department. Captain W. G. Gribbel, of the First Gas Regiment, has returned from active service in France to act as instructor in gas offense.

Dr. Robert P. Fischelis, director of the control department of the H. K. Mulford Co., has entered the Chemical Warfare Service and is now stationed at the control laboratory of the Gas Defense Plant, Long Island City, N. Y.

Dr. A. D. Hirschfelder, of the University of Minnesota, is now with the Research Division of the Chemical Warfare Section and is stationed in Baltimore.

Mr. G. W. Gray, of the Midland Refining Company, El Dorado, Kansas, has been appointed a director of the Bureau of Refining, Oil Division, U. S. Fuel Administration.

Mr. Charles D. Test, formerly chemist for the Western Potash Works of Antioch, Nebraska, has accepted a position on the staff of the United States Tariff Commission.

Mr. Otto Kress, formerly in charge of the research work in pulp and paper at the U. S. Forest Products Laboratory, Madison, Wis., is now director of the new technical dyestuffs laboratory in the dyestuffs sales department of the E. I. du Pont de Nemours & Co., Wilmington, Del.

Major Henry S. Spackman, of the Spackman Engineering Co., Philadelphia, has been promoted to the rank of Lieutenant Colonel in the Engineers Corps, U. S. A. Mr. John E. Schott, formerly an Industrial Fellow at Mellon Institute, has accepted a position with the Experimental Division of the Hercules Powder Co., Kenvil, N. J.

Mr. Phillip Wealey has been appointed manager in charge of the oxyhydrogen plant and sales office of the International Oxygen Co., Pittsburgh, Pa.

Professor E. C. Franklin, of Stanford University, California, is on leave of absence and is engaged in research work for the Nitrate Division, Ordnance Department of the Army. This Division has taken over the experimental ammonia plant and laboratory which has been conducted near Washington by the Department of Agriculture. The work is in charge of R. O. E. Davis and L. H. Greathouse.

Mr. George Quelch, one of the staff engineers of the International Oxygen Co., New York, sailed recently for England to supervise the installation of a 460 cell plant of the I. O. C. Unit Oxyhydrogen Generators for the British Admiralty.

Dr. Alfred J. Larson, assistant professor of chemistry, Carleton College, Northfield, Minn., has been in the chemical service of the Government for a year and was recently commissioned Captain.

Mr. F. K. Bezzenberger, of Harvard University, has been commissioned Captain, and is stationed at Cleveland as gas chemist in the Chemical Warfare Service.

## INDUSTRIAL NOTES

The editorial office of *Paper* and the office of the Secretary of the Technical Association of the Pulp and Paper Industry have moved to 131 East 23rd St., New York City.

The Director of Munitions, Washington, has stopped the construction work at the government air nitrate plant at Ancor, near Cincinnati. Col. Joyes, who was in charge of the work, states that a study is being made to determine the best way to utilize these plants to meet the changed needs of the country.

A contact sulfuric acid plant will be located at Grand Rapids, Mich. The plant is to be situated upon a tract of land which is the property of the United States Government and upon which a picric acid plant is now being erected. When in operation this plant will produce approximately 75,000 net tons per year.

Arrangements have been made by the Subsistence Division of the Quartermaster's Corps whereby the laboratories of the Bureau of Chemistry, Department of Agriculture, throughout the United States are to be more fully utilized by the Army.

The British Board of Trade Journal announces that as potash salts form an essential ingredient in glass making, the very great development which has taken place in the production of British glass would not have been possible had not a parallel development in potash production also taken place.

In view of the need of a permanent exposition of textile and allied industries, a site at San Gines, in the suburbs of Barcelona, Spain, near Catalonia, the center of the textile industries, has been chosen for an imposing edifice for the exposition. The scope of the exposition as planned is both practical and theoretical.

Work has recently been commenced at the salt mines at Buurse, Holland, which is near the German frontier. Previously all the salt for household and industrial needs in the Netherlands was imported from Germany and when these importations stopped there was a great shortage of the commodity.

At a conference on the American potash situation, held October 15 in the office of William Wallace Mein, assistant to the Secretary of Agriculture, in charge of fertilizer control, it was stated that the view of the Department of Agriculture is that the Government should do all that is possible to encourage the production of potash from the cheapest sources in this country in order to enable the farmers to obtain it at a low price, because foreign supplies are now unavailable.

Predictions made a year ago that the deposits of tungsten ore or wolframite in South China would prove to be one of the most important additions to the world's supply of this ore, have been amply fulfilled in the development of the industry. Shipments of the ore from Hongkong alone have totaled \$1,831,590 gold in value so far for the current year. Arrangements have been made by the Conservation and Reclamation Division of the Quartermaster's Corps to take over the disposition and reclamation of waste materials at ordnance depots and arsenals which were heretofore handled by the Ordnance Department. An order has been issued by the Chief of Ordnance directing that all waste products at ordnance stations be turned over to the Conservation and Reclamation officers. Equipment will be installed at the Picatinney Arsenal for the reclamation of empty cast iron and steel shells.

A very fine deposit of kaolin, the fusion point of which is about 3500° F., has been discovered in northeastern Oklahoma by W. T. Croslin, president and chief engineer of the Southwestern Light and Power Transport Co., Miami, Okla.

The first concrete ship built in China, a small ferro-concrete vessel named Concrete, was taken out on trial recently and proved very satisfactory in every way, especially as it was found to be easy to handle.

Due to the difficulties in the shipping situation, England is now utilizing domestic waste material such as fen grass, reed, lumber trimmings, and straw in the manufacture of paper.

Dr. Charles S. Venable, formerly gas chemist at the American University, Washington, is now a captain in the Development Division of the Chemical Warfare Service doing gas offense work in Cleveland.

The largest plant in the world for the manufacture of ammonium nitrate with which to fill high explosive shells is located at Perryville, Md. This government plant which is of concrete construction has all been built since March 4, 1918, and began operations on July 26. It consists of two distinct operating units with a capacity of 300 tons of ammonium nitrate daily. A special commission spent a month studying ammonium nitrate production in England and planned a plant closely resembling the British works.

Proctor & Gamble, soap manufacturers of Cincinnati, have offered to run the New York City garbage plant on Staten Island in order to obtain the 1,000,000 lbs. of glycerin which can be produced there.

Artificial rubber has been made in an experimental way for many years, but it is now reported that the great dye and color works at Elberfeld, Germany, are erecting a large factory for the production of synthetic methyl rubber on a large scale.

Secretary Lane of the Department of the Interior says: "The United States does not need German potash. Germany has thought that she had a whip-hand over America because of her supply of this material, but America can in two years become entirely independent of Germany by the development of her own deposits and the use of the process devised by Dr. Cottrell of this department."

## 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.

## COUNCIL OF NATIONAL DEFENSE

X-Ray Apparatus and Supplies, Part IV. Revised edition of the War Industries Board's list of staple medical and sur<sub>b</sub>ical supplies selected to meet war conditions by Committee on Standardization. 20 pp. Issued September 1918.

## PUBLIC HEALTH SERVICE

An Experimental Investigation of the Toxicity of Certain Organic Arsenic Compounds. G. B. ROTH. Hygienic Laboratory Bulletin 113. Issued July 1918.

On the Toxicity of Emetine Hydrochloride, With Special Reference to the Comparative Toxicity of Various Market Preparations. G. C. LAKE. Hygienic Laboratory Bulletin 113, Part II. Issued July 1918.

#### BUREAU OF CENSUS

Textiles. Report from the Census of Manufacturers, 1914. 165 pp. Paper, 30 cents. This includes a report on production and other data relative to wool manufactures, cotton goods, hosiery, knit goods, silk, textiles, and miscellaneous materials.

## , COMMERCE REPORTS-SEPTEMBER 1918

Owing to increased demands for vegetable oils in the United States, this industry has increased greatly in Japan. The principal oils produced there are soy bean, coconut, rapeseed, cottonseed, and peanut. Of the twenty-five largest plants, all but three use the pressure system; these three use the benzene extraction method. (P. 867)

Efforts are being made to develop the extraction of rubber seed oil in the Malay states. It may be used as a substitute for linseed oil in paint and varnish, and in soft soap. (P. 887)

Manufacture of calcium carbide has been started in South Africa. (P. 915)

The British Scientific Products Exhibition, recently opened, includes exhibits of chemical products and processes, glass, quartz, refractories and porcelain, photographic materials, paper and textiles, and substitutes for petroleum products. Among the chemical products are dyes, laboratory reagents, thymol, aspirin, atropin, and other drugs. (Pp. 936-8)

Among the substitutes for fuel oils and lubricating oils being developed in Sweden are wood-tar oil, sulfite spirits, coal-tar distillates, shale oils, peat-tar oil, etc. (P. 970)

A new fertilizer in use in Italy, known as "tetraogisogate" is made from low grade phosphate rock by heating the powdered rock to 600° to 800° C. with 6 per cent of a mixture of calcium, sodium and magnesium carbonate and a small amount of sodium sulfate. After heating, the product is treated with phosphorous acid, and mixed with sand or dry earth. (P. 1026)

Large phosphate deposits have been discovered on islands near New Zealand. They have been formed by the impregnation of coral deposits by guano from rookeries of sea birds. The phosphate is said to be 85 per cent available. These islands formerly belonged to Germany, but have recently been taken over by Great Britain. (P. 1139) Large deposits of high grade **chromite** have been discovered in South Africa, and are being developed. (P. 1141)

Great efforts are being made in Germany to develop cellulose yarn, made from wood fiber. The product when woven into fabric is strong when dry, but it becomes very weak when wet. (P. 1142)

#### COMMERCE REPORTS-OCTOBER 1918

The manufacture and use of industrial alcohol is increasing in South Africa. Alcohol to be used for motor fuel is to be denatured with 2 per cent by volume of "wood naphtha" and 0.5 per cent of pyridine bases. (P. 59)

A large number of women are now studying chemistry at the German technical schools.  $(P. 6_3)$ 

Abandoned mines of Bohemia are now yielding large quantities of tungsten ore. (P. 63)

The petroleum industry of Mexico is described in detail, giving the location of the fields, and the properties of the fuel oil and other products. (Pp. 84–89)

Steps are being taken to develop nickel deposits in Santo Domingo. (P. 99)

The rubber industry of Ceylon is increasing and areas formerly devoted to cinnamon, rice, tea and citronella are being planted in rubber. (P. 102)

Efforts are being made in Germany to increase the price of **potash**. The domestic consumption has increased and made up in some degree for loss of foreign trade. A large number of prisoners of war and women are employed in the potash mines. (P. 118)

A pure white fiber, obtained from nettles, is being used extensively for textiles in Germany and Denmark. Cloth is being made from peat, with 25 per cent of wool waste. (P. 121)

The British paper industry is now in a serious condition owing to the dependence on foreign sources for raw material. Supplies of rags and esparto have been practically cut off and wood pulp is greatly reduced. Local supplies of straw, grass, and reeds have been utilized. Restrictions to save paper are more drastic than in the United States. Thus, for example, envelopes for official correspondence are used repeatedly by the use of a detachable gummed label for the address. (Pp. 122–5)

Two plants are to be erected in Norway for extracting salt from sea water by electricity (presumably by electrical heating). (P. 165)

It is pointed out in Dutch journals that the German potash industry will, after the war, face severe competition from Cataloma (Spain), Holland, and the United States. (P. 186)

Extensive deposits of iron and nickel ore have been discovered and are being developed in Celebes, Dutch East Indies. It is estimated that there are 350,000,000 tons of lateritic iron ore containing considerable chromium and nickel, and a large amount of ore containing 25 per cent of nickel. (P. 196)

It is expected that deposits of tungsten ore in Sweden will supply all Sweden's needs for 20 years. (P. 196)

A survey of the potash situation in Great Britain shows that the following sources of supply are actually meeting the demands: blast furnace dust, kelp, wool grease, and cement. It is estimated that 50,000 tons of potash can be obtained annually from the blast furnaces, with almost no additional cost, except for the small amount of sodium chloride added to the charge. The British Potash Company is one-half controlled by the government and one-half by the public. All blast furnace dust is under government control. (Pp. 198–200)

The manufacture of lithopone has been started in Italy. (P. 202) Large amounts of tungsten ore are being exported from Hongkong. (P. 216)

A marked increase is noted in the imports of American dyestuffs into Japan. (P. 247)

It is reported that synthetic rubber is being manufactured successfully at Elberfeld, Germany. (P. 265)

By a new "cold" process paper pulp is being made in England from straw yielding 65 per cent of pulp instead of 40 per cent by the soda process. The new pulp will not bleach white, but it may be used up to 10 per cent in newsprint paper, of which it actually increases the strength. (P. 280)

A new explosive known as "sengite" is made in South Africa by the addition of sodium nitrate to guncotton. Considerable water may be left in the pressed mixture without decreasing its blasting power, but increasing its stability on handling. (P. 282)

The cellulose industry of Sweden shows a marked increase, especially of sulfite pulp. (P. 326)

Manganese ores are now being produced in Chihuahua, Mexico, in large quantities, and exported to the United States. The manganese content is from 40 to 48 per cent. (P. 356) Paper yarn for textiles is now being used extensively in Germany where 88,000,000 lbs. per year are produced. Thread is being made which is suitable for coarse sacks, etc., but no fine threads. (P. 358)

Exi	PORTS TO THE UNITED ST.	ATES
SAMOA-Sup. 62a	FRANCE-Sup. 5d	CEVLON (P. 213)
	Aluminum	Citronella oil
Copra	Bones	Croton seeds
Hides	Carbon	Papain
Rubber	Saffron	Graphite
	Casein	Rubber
JAPAN-Sup. 55b	Glass	
A. AND A DOMESTIC STREET, AND A DOMESTIC AND A DOMESTICAL AND A A DOMESTICAL AND A DOMES	Hides	Vanilla
Graphite		DUTCH EAST INDIES-
Bean oil	Essential oils	Sup. 53a
Potato starch	Olive oil	
Vegetable wax	Peanut oil	Copra
	Paper stock	Damar
HONDURAS-Sup. 31b	Platinum	Gambier
particles in a second second in a post strate that was a first fact of a second	Zinc ore	Hides
Balsam	NICARAGUA-Sup. 34a	Kapok
Liquid amber	Balsam	Coconut oil
Copra	Copper	Quinine
Hides	Fustic	Rubber
Indigo	Gold '	Tin
Antimony ore	Hides	Platinum
Gold ·	Rubber	Paraffin
Silver	Silver	Indigo
Sarsaparilla	Sugar	
State States - Real To		

# BOOK REVIEWS

Organic Compounds of Arsenic and Antimony. By GILBERT T. MORGAN, D.Sc., Professor of Applied Chemistry, City and Guilds Technical College, Finsbury. 8vo., 376 pp. Longmans, Green & Company, London, England, 1918. Price, \$4.80 net.

In this monograph Dr. Morgan presents in a well systematized manner the chemistry of the organic compounds of arsenic and antimony. The work as a whole discusses the development of this most complicated, but most interesting field of organic chemistry from the earliest discoveries to the most modern, including an account of all researches up to the end of 1917.

In the introduction the author gives a brief review of the more important discoveries, in their historical order, which have brought the chemistry of the arsenicals into its present important position in relation to medical science and the theory of chemistry.

In Chapter IV the author, starting with the classic work of Bechamp, develops the chemistry involved in the preparation of atoxyl and its closely allied derivatives; in Chapters V, VI, and VII he describes the developments which led to the discovery and use of salvarsan and neosalvarsan, and the more modern arsenicals, luargol, gallyl, etc. The detail of their preparation, as well as the chemistry involved, and the discussion of their use in the medical field are given.

In the later chapters the author treats of the preparation and properties of the more important organic compounds of antimony. In the appendix a discussion of the analytical methods for the determination of arsenic and antimony in their organic combinations is given, also a complete and accurate bibliography of the publications on the organic arsenicals and antimonials arranged in chronological order. The use of graphic formulas throughout the work to illustrate the constitution of these compounds and their relation one to another does a great deal towards helping the reader to a clear understanding of the subject.

The appearance of this book, the only complete and modern treatise on this subject in the English language, should be most welcome.

#### J. B. CHURCHILL

The Chemical Engineering Catalog—1918 Edition. 836 pp. Illustrated. Price, \$5.00, or obtained by special arrangement with the Publishers, The Chemical Catalog Co., Inc., New York City.

One of the features of the Fourth National Exposition of

Chemical Industries was a booth piled high with the volumes of the 1918 edition of the Chemical Engineering Catalog, ready for distribution, as a loan without cost, "to any Chemical Engineer, Chief Chemist, Industrial Plant Superintendent, Works Manager, Buyer, or Head of a Chemical Department in a University or College." The piles rapidly disappeared. Congratulations to the publishers upon the prompt appearance of this veritable Exposition in itself, in type and cut!

That the Chemical Catalog has proved its usefulness to the industry is attested by the following figures:

	Catalog	Directory	No. of Firms Using	Maximum No. Pps. to	No. of Copies
Year	Pages	Pages	Space	One Firm	Printed
1916	. 205	74	132	8	8500
1917	. 347	154	247	18	8500
1918	. 578	210	439	20	10200

As in previous years, the volume is published under the supervision of a committee appointed by the American Institute of Chemical Engineers, the American Chemical Society, and the Society of Chemical Industry. This committee for the 1918 volume consisted of Messrs. Charles F. McKenna, *Chairman*, L. H. Backeland, M. C. Whitaker, Raymond F. Bacon, William M. Grosvenor, Gustave W. Thompson, and William H. Nichols.

The present volume shows a large increase in the Chemicals and Materials Section, and a similar growth in the Equipment Section, including "pumps, packing, valves, and fittings of all kinds for the handling of steam, air, and liquids; belting, power transmission equipment, conveying, hoisting, and transporting machinery, etc."

For the first time a technical book department has been included, and a book purchasing service is offered the users of the Catalog.

The editors, with every reason to be proud of their achievement, waste no space in idle boasting, but frankly recognize the possibilities of error in so comprehensive a publication, and ask for friendly criticism and corrections.

The Catalog is an exemplification of the growth of the chemical industry and will be constantly consulted by those who bear the responsibility for further development of that industry.

CHAS. H. HERTY

## NEW PUBLICATIONS

#### By CLARA M. GUPPY, Librarian, Mellon Institute of Industrial Research, Pittsburgh

- Butter: Book of Butter; A Text on the Nature, Manufacture and Marketing of the Product. E. S. GUTHRIE. 12mo. 270 pp. Price, \$1.75. The Macmillan Co., New York.
- Chemical Directory: Annual Chemical Directory of the United States. B. F. LOVELACE AND C. C. THOMAS. 2nd Ed. 8vo. 534 pp. Price, \$5.00. Williams and Wilkins, Baltimore.
- Chemistry: Calculations of Inorganic Chemistry and Qualitative Analysis. ALEXANDER SMITH AND W. C. MOORE. 12mo. 106 pp. Price, \$1.00. The Century Co., New York.
- Chemistry: Future of Pure and Applied Chemistry; Presidential Address Delivered at the Annual General Meeting of the Chemical Society, March 21, 1918. W. J. POPE. 8vo. 12 pp. Chemical Society, London.
- Chemistry: Outlines of Theoretical Chemistry. F. H. GETMAN. 2nd Ed. Revised and enlarged. 8vo. 539 pp. Price, \$3.50. John Wiley and Sons, Inc., New York.
- Chemistry: Précis de Chimie Industrielle. PIERRE CARRÉ. 976 pp. Price, 16 fr. 50. Baillière et Fils, Paris.
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## **MARKET REPORT-NOVEMBER, 1918**

WHOLESALE PRICES PREVAILING IN THE NEW YORK MARKET ON NOVEMBER 16, 1918

## INORGANIC CHEMICALS

Acetate of Lime100 Lbs.		nomina	1
Alum, ammonia, lump100 Lbs.		7.00	
Aluminum Sulfate, (iron free)Lb.	4.50	0	4.75
Ammonium Carbonate, domesticLb.		nomina	
Ammonium Chloride, whiteLb.	19	0	20
Aqua Ammonia, 26°, drumsLb.		nomina	
Arsenic, whiteI.b.		1/4 @	17
Barlum ChlorideTon	70.00	0	80.00
Barium NitrateLb.	12	0	14
Barytes, prime white, foreign	30.00	0	35.00
Bleaching Powder, 35 per centLb.	41	A provide the second state	5
 Blue VitriolLb.	91	Contract of the second second	91/4
Borax, crystals, in bagsLb.		1. @	101/6
Boric Acid, powdered crystalsLb.		/4 @	81/4
Brimstone, crude, domesticLong Ton	I	ominal	
Bromine, technical, bulkLb.	75	0	
Calcium Chloride, lump, 70 to 75% fusedTon	20.00	0	22.00
Caustic Soda, 76 per cent100 Lbs.	3.90	Ø	4.10
Chalk, light precipitatedLb.	43	and the Western of the V	5
China Clay, importedTon	20.00	0	30.00
FeldsparTon	8.00	0	15.00
Fuller's Earth, foreign, powdered		nomina	
Fuller's Earth, domesticTon	20.00	0	30.00
Glauber's Salt, in bbls100 Lbs.	2.10	0	3.00
Green Vitriol, bulk100 Lbs.	2.00	0	2.25
Hydrochloric Acid, commercial, C. PLb.		nomina	
Isdine, resublimedLb.	4.25	0	4.30
Lead Acetate, white crystalsLb.	17	0	18
Lead Nitrate, C. PLb.		85	
Litharge, AmericanLb.	14	0	15
Lithium CarbonateLb.		1.50	
Magnesium Carbonate, U. S. PLb.	20	0	30
Magnesite, "Calcined"Ton	60.00	0	65.00
Nitric Acid, 40°Lb.		73/4	
Nitric Acid, 42°Lb.		81/1	
Phosphoric Acid, 48/50%Lb.	71/2	0	9
Phosphorus, yellowLb.	1.10	õ	1.15
Plaster of ParisBbl.	2.00	ĕ	2.50
Potassium BichromateLb.	44	0	46
Potassium Bromide, granularLb.	1.25	Ø	1.30
Potassium Carbonate, calcined, 80 @ 85% Lb.	35	0	
Petassium Chlorate, crystals, spotLb.	40	0	41
Petassium Cyanide, bulk, 98-99 per cent Lb.		nomina	1
Potassium Hydroxide, 88 @ 92%Lb.	60	0	70
Potassium Iodide, bulkLb.	3.75	0	4.00
Potassium NitrateLb.	27	0	30
Potassium Permanganate, bulk, U. S. PLb.	1.75	0	1.95
Quicksilver, flask75 Lbs.	125.00	0	130.00
Red Lead, American, dry 100 Lbs.	11.25	0	11.50
Salt Cake, glass makers'Ton	17.50	0	22.00
Silver NitrateOz.	631		65
Seapstone, in bags	10.00	0	12.50
Soda Ash, 58%, in bags100 Lbs.	2.60	0	2.70
Sodium Acetate, broken lumpLb.	20	@	21
Sedium Bicarbonate, domestic100 Lbs.	4.10	0	4.25
Sodium BichromateLb.	20	0	221/2
Sodium ChlorateLb.	25	0	251/1
Sødium CyanideLb.	32	0	35
Sodium Fluoride, commercialLb.	17	0	18
Sodium Hyposulfite100 Lbs.	2.60	@	3.60
Sodium Nitrate, 95 per cent, spot100 Lbs.	4.421	1:0	5.00
Sodium Silicate, liquid, 40° Bé	31		31/1
Sodium Sulfide, 60%, fused in bblsLb.	11	0	12
Sodium Bisulfite, powdered	12	0	14
Strontium NitrateLb.	25	0	30
Sulfur	2.25	Ø	4.60
Sulfuric Acid, chamber 66° Bé		18.00	
Sulfuric Acid, oleum (fuming)		32.00	
Talc, American white		15.00	
Terra Alba, American, No. 1		1.171/2	
Tin Bichloride, 50°Lb.	28	@	30
Tin OxideLb.	90	0	1.00
White Lead, American, dryLb.	10	@	101/1
Zinc CarbonateLb.	18	0	20
Zine Chloride, commercialLb.	15	Ø	151/1
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OPGANIC CUPRITCALS			

ORGANIC	CHE	MICALS
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Acetanilid, C. P., in bblsLb.	65	0	70	
Acetic Acid, 56 per cent, in bbls100 Lbs.	9.30	0	9.55	
Acetic Acid, glacial, 991/1%100 Lbs.	19.50	0	19.70	
Acetone, drumsLb.	251/	3 @		
Alcohol, denatured, 180 proofGal,	68	0	69	

Alcohol, sugar cane, 188 proofGal.	4.90	4.95
Alcohol, wood, 95 per cent, refinedGal.	911/1 @	
Amyl AcetateGal.	4.20 @	
Aniline Oil, drums extraLb.		
	30 @	
Benzoic Acid, ex-toluolLb.	3.00 @	
Benzene, pureGal.	22 @	221/1
Camphor, refined in bulk, bblsLb.	1.241/1 @	1.25
Carbolic Acid, U. S. P., crystals, drumsLb.	42 @	45
Carbon BisulfideLb.	9 Ø	10
Carbon Tetrachloride, drums, 100 galsLb.	nomi	nal
ChloroformLb.	63 @	70
Citric Acid, domestic, crystalsLb.	1.12 @	1.20
Creosote, beechwoodLb.	2.00 @	2.10
Cresol, U. S. PLb.	19 @	20
Dextrine, corn (carloads, bags)Lb.	8 0	.9
	nomi	
Dextrine, imported potatoLb.	A CONTRACTOR CARE LONG TO A	States and the state of the states
Ether, U. S. P. 1900Lb.	27 @	30
Formaldehyde, 40 per centLb.	DI L'ALER HAR AND A STATE OF	ov't price
Glycerine, dynamite, drums extraLb.	e 60 Ø	62
Oxalic Acid, in casksLb.	41 @	43
Pyrogallic Acid, resublimed, bulkLb.	3.25 @	3.50
Salicylic Acid, U. S. PLb.	85 @	95
Starch, corn (carloads, bags) pearl100 Lbs.	6.00 @	7.00
Starch, potato, JapaneseLb.	13 @	14
Starch, riceLb.	121/2 @	13
Starch, sago flourLb.	91/4 @	103/4
Starch, wheatLb.	nomin	
Tannic Acid, commercialLb.	65 @	80
Tartaric Acid, crystalsLb.	85 @	87
OILS, WAXES, ETC.		
oins, waads, alo.		
Beeswax, pure, whiteLb.	. 63 @	65
Black Mineral Oil, 29 gravityGal.	24 @	25
	the second s	23
Castor Oil, No. 3Lb.	35	
Ceresin, yellow	17 @	18
Corn Oil, crude100 Lbs.	16.75 @	17.75
Cottonseed Oil, crude, f. o. b. millLb.	171/1 @	K. contraction
Cottonseed Oil, p. s. y100 Lbs.	21.00 @	22.00
Menhaden Oil, crude (southern)Gal.	i.15 @	1.25
Neat's-foot Oil, 20°Gal.	3.45 @	3.55
Paraffin, crude, 118 to 120 m. p Lb.	93/4 @	10
Paraffin Oil, high viscosityGal.	40 @	41
Rosin, "F" Grade, 280 lbsBbl.	15.10 @	15.20
Rosin Oil, first runGal.	75 @	76
Shellac, T. NLb.	68 @	70
Spermaceti, cakeLb.	31 @	33
Sperm Oil, bleached winter, 38°Gal.	CONTRACTOR AND A CONTRACTOR OF A CONTRACTOR AND A CONTRACTOR	2.25
	and the second second second second	
Spindle Oil, No. 200Gal.	38 @	40
Stearic Acid, double-pressedLb.	24 @	25
Tallow, acidlessGal.	1.58 @	1.60
Tar Oii, distilledGal.	36 @	38
Turpentine, spirits ofGal.	65 @	661/2
the second day and in the second		
METALS		
Aluminum, No. 1, ingotsLb.	33 @	34
Antimony, ordinaryLb.	131/4 @	14
Bismuth, N. YLb.	3.50 @	3.65
Copper, electrolyticLb.	26 @	
Copper, lakeLb.	26 @	
Lead, N. YLb.	8.05	
Nickel, electrolyticLb.	55 Q	56
Platinum, refined, softOz.	the second s	
Silver	nomin	
SilverOz.	1.011/8	
Tin, StraitsLb.	nomina	
Tungsten (WO2)Per Unit	20.00 @	24.00
Zinc, N. Y	9.40 @	9.60
And a state of the second second second	Linke Marin	
FERTILIZER MATERIAL	8	
Ammonium Sulfate	4.75 @	Marriso 193
Blood, dried, f. o. b. New York Unit	4.75 @	7 50

Ammonium Sultate	4.75	0		
Blood, dried, f. o. b. New YorkUnit	7.40	0	7.50	
Bone, 3 and 50, ground, raw	37.00	0	37.50	
Calcium CyanamideUnit of Ammonia	1	omin	al	
Calcium Nitrate, Norwegian		-		
Castor MealUnit				
Fish Scrap, domestic, dried, f. o. b. works Unit	7.25	and	20c	
Phosphate, acid, 16 per cent	17.50	0	18.00	
Phosphate rock, f. o. b. mine: Ton	The second se	omin	๗	
Florida land pebble, 68 per cent	5.00	0	6.00	
Tennessee, 78-80 per cent	7.00	0	8.00	
Potassium "muriate," basis 80 per cent Ton	300.00	0	310.00	
Pyrites, furnace size, importedUnit	the state of the s	uominal		
Tankage, high-grade, f. o. b. Chicago Unit	6.75	0	6.80	