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EDITORIALS

The Prize Essay Contest

CHEMISTS have a splendid opportunity for service in carrying out the details of the prize essay contest made possible by a gift on the part of Mr. and Mrs. Francis P. Garvan to encourage the study of chemistry so that the youth of the land may appreciate what the science is doing for our everyday life. Six topics have been chosen by the committee, and the first prize of a twenty dollar gold piece with a certificate will be awarded in each state and the District of Columbia for the best essay within these geographical areas on each topic. Undoubtedly, efforts will be made within the various states to provide inducements for further study in the form of scholarships in the institutions of higher education. From among the state winners a national committee, to be announced later, will select the winners to receive the four-year scholarships at Yale or Vassar. These scholarships carry $500 a year and tuition, and were made possible by the generosity of Mr. and Mrs. Garvan.

This is not all the story, for to insure access to suitable literature, the reading of which will stimulate the imagination of contestants and indicate methods of attacking their problem, Mr. Garvan has provided for the distribution of more than ten thousand sets of five books each, these to be sent to the accredited secondary schools, both public and private, without so much as a request. A number of sets will also be deposited with libraries prepared to facilitate their circulation, and we prophesy that the coming winter will see a wider demand for and a more extensive reading of popular literature on chemical subjects than ever before. We all recognize that in the boys and girls lies our greatest opportunity to encourage chemistry. This does not mean that we expect all high and secondary school students to become chemists. It does mean that attention will be drawn to chemistry as a cultural study, that a wider view upon everyday affairs will be obtained, and that chemistry will be placed in the popular estimation, on a par with astronomy, for example, which has obtained a big hold upon the layman.

This is the first nation-wide plan of this kind to be evolved. In accepting its administration the SOCIETY has assumed a real responsibility. It is a call to the individual chemist as well as to the organized sections to recognize their responsibility in the successful completion of the work. Everything possible is being done to bring the contest before the boys and girls, and we must expect frequent calls for assistance in recommending literature, sometimes in discussing the chemical work, and perhaps in arranging for visits to plants utilizing chemistry in some of its phases. There will doubtless also be a large number of essays to be seriously considered in the competition. In fact, it is difficult to predict all the ways in which some service may be required. While the prizes are to be awarded to students of high school grade, much of the benefit of the contest will eventually accrue to chemists and their science. We therefore have a direct interest in the success of the contest.

A prize essay committee has been organized, with the secretary equipped to handle inquiries which chemists and others may care to make. There will be ample explanatory literature for distribution, and it is hoped that adequate and proper publicity for our effort may be obtained. It is another opportunity for chemists to show the value of their organization. The work at its inception holds promise of marked success.

The American Chemical Prize

WHEN Dr. Smith announced at Pittsburgh that the Allied Chemical and Dye Corporation through William H. Nichols as spokesman had founded an annual prize of $25,000, the Council wisely chose a committee consisting of Edgar F. Smith, E. W. Morley, C. F. Chandler, F. P. Venable, and Ira Remsen, to collaborate with representatives of the corporation in arranging the necessary details. Shortly before the New Haven meeting the death of Dr. Morley was announced and Theodore W. Richards has taken his place upon the committee. The committee was not ready to report at New Haven and the Council eagerly awaited its report at Milwaukee. The magnificent prize will be known as

THE AMERICAN CHEMICAL PRIZE

(Founded by the Allied Chemical and Dye Corporation)

and "will be awarded annually to that chemist, man or woman, a citizen or resident of the United States of America at the time, who in a certain year or through a period of years has made a contribution of high merit or in some marked way has promoted the betterment of society through the science of chemistry."

Our committee is to designate the additional members of the AMERICAN CHEMICAL SOCIETY upon the jury of award, and as soon as this jury can be completed and agree upon recommendations the first recipient of the prize will be announced. This recognition of outstanding work in chemistry cannot fail to benefit chemistry in America to a degree in comparison with which the monetary reward to the chemist is insignificant. Somehow, for the encouragement of the large number of chemists who now work faithfully in obscure places, we hope the first to receive this prize will be some one who has labored in a little-known laboratory with inadequate facilities. We should like to see it demonstrated that a man with native ability and steadfast purpose can achieve things even though he does not have the advantages obtained in large institutions and centers of population. We should also like to see one of the younger men encouraged in his work, as an indication that the prize is not to go necessarily to the older members of the profession and to dispel the idea that in addition to outstanding work a man must attain years before he can win full recognition.

Long after those who have been instrumental in the foundation of this annual prize have passed on, the science and the general public will continue to reap the harvest. The thanks of chemists are properly due to William H. Nichols, a past president of our SOCIETY, an honorary member, and the recipient of many scientific honors, who has acted as spokesman for the Allied Chemical and Dye Corporation in this matter. As for our committee, nothing that can be said here would add to the frequent expressions of the debt of gratitude that American chemists owe the members of the committee for their continued work which has done so much in the past, as in the present, to bring chemistry to the forefront and maintain America's position as a nation unsurpassed in its modern chemical achievement.

In Duncan's Footsteps

ACCORDING to the best of our information it was the late Robert Kennedy Duncan who, in modern times, emphasized the necessity of popularizing our science in order to win that sympathetic appreciation on the part of the public which we must have if fundamental research and even the industrial application of its results is to have support upon an adequate scale. The "Chemistry of Commerce" and other works by Duncan are classics, and form the nucleus of a growing series of publications which are not only valuable to us as chemists, but which have attracted so wide a circle of nontechnical readers as to make them commercially attractive to the publishers.

Interest in the popularization of science on the part of those charged with public responsibility is manifest in the message upon the cover of our September issue, which was especially prepared for *Industrial and Engineering Chemistry* by the Secretary of Commerce, and shows an appreciation for science which until lately has been unique among public men.

The women of the country are becoming increasingly interested in the application of science to everyday life. Those who heard Mrs. Winter at the General Meeting at Milwaukee could not fail to be impressed by her plea for further simplification of scientific facts to facilitate their assimilation by the intelligent lay reader. She offered the coöperation of the efficient organizations of American women if chemists will do their part in preparing the results of their labors, their plans for the future, and statements concerning the significance of their work, so they may be comprehended without previous training in the science.

The newspapers must consider the desire of the public in preparing copy for their numerous editions, and subjects not considered news are practically debarred from their columns. We doubt if any organization has ever obtained more desirable space in first-rate newspapers than was accorded the AMERICAN CHEMICAL SOCIETY in connection with the Milwaukee meeting. We seem to have passed the stage when a few inches tucked away on an inconspicuous page was considered adequate by the editor. We are frequently given preferred space, and our stories are carried on different pages of the same edition.

We, who are committed to the popularization of our science through the publication of authentic but nontechnical articles, are further encouraged by the steadily changing attitude of those who confine their efforts to researches in pure science. In this group are the representatives of sciences other than chemistry who have come to realize that, to some extent at least, the present position of chemistry in America is due to the willingness of even our most renowned chemists to have the public understand their work.

All of which means that something is happening. The public is asking for chemical information. The daily press is making a greater effort to study that demand, and the extent to which we may go in securing publicity depends wholly upon the coöperation which the chemist gives, not only to our A. C. S. News Service, our News Edition, and the publicity committees of local sections, but to the individual reporter bent upon serious inquiry. Sometimes we cannot approve the headlines employed, but these are becoming more satisfactory and, after all, are not so objectionable as would be an omission of authentic chemical information from the daily press.

We have established an enviable reputation in the popularization of science and our influence can be greatly extended with your hearty coöperation.

An Appeal for Opinions

TIME after time the Council of the SOCIETY creates a committee of busy men and charges them with the duty of formulating plans or making decisions upon questions of vital interest to the life and growth of our organization. Having created the committee, members of the SOCIETY forget their responsibility in its work, and as a consequence may be disappointed in the committee's report when it appears. We know that in many localities men are devoting a great deal of thought to questions now before the SOCIETY, but for some unexplained reason results of their deliberations are too seldom registered with those who endeavor to serve the SOCIETY. We wish to appeal to sections and individuals to send their criticisms and suggestions to the committees seeking information. Two of the committees continued—namely, those on intersectional meetings and the classification of membership—have before them questions which merit prolonged discussion. These questions should be discussed by the local sections and their recommendations transmitted through the executive committees. In no other way will committees be able to discharge their duty as they see it and perform the service which they desire to render. There are more than sixty-five sections in the AMERICAN CHEMICAL SOCIETY, and the Committee on Intersectional Meetings has heard from but twenty-nine. The Committee on Prize Essays has also appealed to various local sections for recommendations with respect to the personnel of state committees and other details. The response has been far from complete.

These and other questions should be placed upon the program of each local section for early consideration and discussion. Do not let the matter end with discussion. By all means transmit to the appropriate committee or individual specific opinions containing suggestions along definite lines and, where possible, complete plans for consideration. In the case of questions requiring sectional action, communications should be official and not merely the expression of individual ideas.

Earning Power of Research

ORIGINALLY, the lead from which cable sheaths are made was given a 3 per cent admixture of tin to obtain the necessary mechanical properties in the alloy. About twelve years ago the price of tin advanced, while the increase in the quantity required for new telephone cable construction became so large that research was called upon to provide a substitute. As a result new sheaths contain one per cent of antimony and in ten years the new formula has earned a saving approximating $6,000,000.

Another important metallurgical result was an improved contact metal used in the millions of relays and tiny switches required in telephone plants and central stations. Since 1916 this new metal has earned through savings about $13,000,000.

Another illustration of the earning power of research taken from the experience of the Bell system is the use of so-called phantom circuits. A simple circuit consists of two line wires. In phantoming it is possible to superimpose a third circuit upon two pairs of such wires, utilizing each pair as if it were a single line wire. At present there are about 400,000 miles of phantom circuit in the Bell system. The cost involved in obtaining these phantom circuits was about $9,000,000, but the cost of the additional copper wire necessary to string simple circuits to do this work would have been $90,000,000.

These earnings are real and the income upon the investment in research which makes them possible is greater than that usually obtained in commercial ventures.

Minimizing Human Error

THOSE who have been for long associated with the scientific apparatus and supply business know how continually Americans have been told that it would be impossible, for three principal reasons, to produce precise ware in this country. These reasons are fundamental characteristics which differentiate American business methods from those of most other countries, and upon two of these the success of many an American enterprise has to a large extent depended. First, our standards of living make high wages necessary in practically every line of our activity. Second, to compete successfully with this unavoidable high cost, we have developed automatic or semi-automatic machinery to an unusually high degree. Third, the manufacture of precise scientific instruments requires a patience and diligence, not to say an actual love of one's work, which unfortunately has never been characteristic of the American worker. But those who assured us that precision glassware, for example, would never be made in America, did not take into account American genius in providing mechanical devices which would be almost human in their movements, and which would not only minimize errors of the workman, but provide a substitute for an extreme accuracy which they thought impossible in America.

We are accustomed to think of "shoes and ships and sealing wax," automobiles, typewriters, sewing machines, etc., as standardized and produced in immense quantities, but it has taken Americans to standardize and produce in quantity such an article as an analytical buret of precision. A recent visit to a plant in Vineland, N. J., impressed us most of all with the great genius displayed in minimizing human errors and in attaining a quantity production of precise apparatus which makes it more nearly possible to compete with low wage standards of other countries and to surpass in quality apparatus formerly made solely by hand.

We used to marvel at the skill of the glass-blower who was able to produce standard lengths of tubing, fairly uniform in diameter and thickness of wall, but here is a mechanical device which works continuously and draws tubing to a given size varying not more than 0.2 mm. in diameter and 0.02 mm. in thickness of wall, without striae or air bubbles. Such tubing is blown by the mile and is cut in specified lengths by an automatic machine as it cools.

To be sure, the graduation of a buret made from such an ideal piece of straight tubing is comparatively simple, and yet to do this mechanically, making allowances for slight but inevitable variations, even in machine-made tubing, is an accomplishment worthy of note. The tubing is first fitted with a stopcock and is then coated with wax upon which the engraving is done prior to etching. Bench marks are placed at intervals on the basis of weighed mercury fillings. This part of the process is carried out by an expert operative, using all possible mechanical aids. The tube is next put into the automatic grading machine upon which adjustments are made so that the major divisions coincide accurately with those previously determined. Each interval is automatically graduated with the same number of divisions, and in this fashion error is practically eliminated. The etching of the glass and the removal of the wax, followed by filling the etched marks with color, is but a detail.

The marked success with which ware made in this fashion meets the requirements of the Bureau of Standards is ample evidence of the success of the process. It has taken much expenditure of patience, energy, and capital to achieve what now appears simple. It shows the determination of some Americans never again to be dependent for essentials upon other sources, and if we are so constituted as a people that we compete with difficulty where the work is tedious and oftentimes uninteresting, we appear to have the ability to create machines which will do such labor for us. It is a piece of work undertaken in a field where the monetary returns are not large and the volume of business is never great, but it indicates a spirit which we appreciate and applaud.

Where Lies the Difficulty?

WE HAVE received several comments upon a "want ad" by a member of the SOCIETY which appeared in a recent number of the News Edition.

The following is taken from one of these letters:

> What is wrong with our profession when its younger members insist upon advertising themselves for work "salary unimportant," etc.? (I won't go through the list.) Are we not the doctors of the material world? Has not every trouble in the material world a chemical foundation? Why, then, are the chemists the poorest paid, the worst treated, the most ignored of professional men? Do we act like professional men?
>
> Does the college professor's influence rob the profession of the wage demands its members should make? Does the smallness of the college professor's salary cause him to advise his students to accept niggardly terms? Or, are the graduates and chemists of no greater value than the salary they now earn? Are there too many chemists or too many so-called "chemists?" Does the individual chemist dispense his knowledge too readily to the laymen with the desire to appear learned, forgetting that he is robbing his brother chemists of their wage? * * *
>
> Has professional dignity and disdain for monetary matters dragged the profession down? Probably there are many men who work for science's sake alone, without any thought of using their knowledge as a means to a livelihood, but the great advances in technical work have been made by men whose bread, butter, and position depended upon their getting results.
>
> I know you cannot answer these questions, nor do I expect you to do so. Most of them may be far-fetched. However, I feel that a real problem exists and that something should be done to solve it. We who are in responsible positions should shoulder some of the problems of the under dog, because we are no doubt in some sense responsible for his state of being. It is not an impossible task. The physicians have a dignified profession and yet they charge for it, their elevation in the laymen's mind increasing with their increase in rates.
>
> Why, then, must chemists advertise themselves as willing to work for nothing or almost nothing? Are our graduates so narrowly trained that they can do only one kind of work? Are they single-tracked? Are they afraid of work? Have they been disillusioned? At any rate, after a chemist (a real chemist) has served an apprenticeship of some years, should not his average salary compare favorably with that of men in other professions? How are we going to get rid of the ne'er do wells?

As our friend states, we cannot attempt to answer all these questions. Graduation signifies, not the completion of one's education, but its commencement. The college course is a success if it equips a man so that he can grasp facts readily, know sources of reliable information, and segregate truth from the mass of material offered to him. Because he can do these things the graduate chemist is worth a fair wage and only a fair wage until he begins to become acquainted with the detailed work of his employer. No doubt the employer feels that the experience gained by the chemist should be reckoned as a part of his remuneration; but in too many cases the chemist is kept too long on probation. He should be promoted in a substantial manner, given to understand that such promotion has not been earned, or replaced within a reasonable time. Nothing is so deadening as uncertainty.

The Priestley Medal

THE award of the Priestley Medal to Ira Remsen is another evidence of the work originally undertaken through the enthusiasm of the late Francis C. Phillips. The Priestley Medal is an important award. It is a distinct honor which will be conferred once in three years in accordance with the rules established by the Priestley Medal Committee. This committee has done valuable work in assembling letters, apparatus, and books of Joseph Priestley, and placing much of this material in the old home at Northumberland, Pa., which is being restored as a result of the committee's further activity. There is also the portrait of Priestley presented to the National Museum in Washington, and now this gold medal which will be more and more highly prized as its import is understood. We congratulate Dr. Remsen, who is the first recipient of the medal, and believe its triennial award will be a further incentive to chemists to put forth their best efforts.

MILWAUKEE MEETING

THE events of the short five days occupied by the Sixty-sixth Meeting of the AMERICAN CHEMICAL SOCIETY held at Milwaukee, Wis., September 10 to 14, inclusive, can be recorded in comparatively little space, but only time can record the far-reaching effect which the developments at Milwaukee will have upon the future of American chemistry.

In summarizing, briefly, the outstanding features of the meeting, first place must be given to the two prize awards which will be sponsored by the AMERICAN CHEMICAL SOCIETY as a result of the generous gifts of the Allied Chemical and Dye Corporation on the one hand and Mr. and Mrs. Francis P. Garvan on the other. Stimulation for both the workers in chemistry and those who are about to begin a career is provided through these two magnificent prize offers.

Next in order of importance perhaps was the splendid scientific showing made by the SOCIETY through the work of its divisions and sections, which provided a total of more than three hundred papers on a wide range of chemical and allied subjects. Not only were these papers of intense interest to the assembled members, but many of them furnished interesting newspaper stories, thus keeping the work of the SOCIETY before the public.

The great interest displayed by college men, as well as those identified with the industries, in the subject of chemical education and the general recognition that the future of chemistry depends largely upon the training of the coming chemist, as well as the desire of all to make this training as effective as possible, might well be characterized as another outstanding feature of the meeting.

The award of the first Priestley Medal to Dr. Ira Remsen; the public meeting at which Mrs. Thomas G. Winter, president of the General Federation of Women's Clubs, delivered an address full of practical suggestions for bringing chemistry home to the public; the trip to Madison, Wis.; and lastly, the splendid manner in which the convention was handled by the local committee completes the brief survey of outstanding features, but by no means describes the various other items of business and scientific interest which transpired. Entertainments for all and especially for the ladies were provided most lavishly by the local hosts.

Following the council meeting on Monday, the meeting was formally opened Tuesday morning in Plankinton Hall of the Municipal Auditorium. Clare H. Hall, the chairman of the local section, presided. Welcoming addresses were made by Mayor Daniel W. Hoan, State Senator Oscar Morris, and President Albert C. Fox of Marquette University. President Franklin responded for the SOCIETY, after which two general addresses were delivered. Charles F. Burgess, director of the C. F. Burgess Laboratories, spoke on "Marketing Chemical Discoveries," and Dean Arthur I. Kendall, of the Medical School of Northwestern University, spoke on "Bacteria and the Chemist."

Special general divisional programs arranged by the Divisions of Physical and Inorganic Chemistry, Organic Chemistry, and the Section on Chemical Education occupied the afternoon of the first general meeting day. In the evening a dinner and entertainment were provided which turned the thoughts of those present from science to sociability, and a very enjoyable evening was spent.

All the divisions and sections met some time Wednesday or Thursday, and some on both days. Symposia on "Bread," "Soils, Fertilizers, and Crops," "Synthetic Methods," "Gelatin," "Chemistry of Glandular Products," "Activated Sludge," and "Biological Chemistry" were held in connection with several of the divisional meetings.

The Section on Chemical Education held a joint meeting with the Division of Industrial and Engineering Chemistry and the Milwaukee Chamber of Commerce. While few of the last group attended the meeting, the main object was accomplished, because educators and industrialists were provided with an opportunity to air their views, which they did, and a wholesome coöperative effort will very likely result.

Mention has already been made of two features of the public meeting on Wednesday evening. The closing number on the program of the meeting was an address by President E. C. Franklin on "Systems of Acids, Bases, and Salts."

The trip to Madison, Wis., including inspection of the University of Wisconsin buildings and the Forest Products Laboratory, proved to be very delightful to the one hundred and fifty or more who spent Friday as the guests of the Wisconsin Section. Industrial excursions in Milwaukee had been provided for those not desiring to make the trip to Madison.

Newspapers of Milwaukee were quite generous with their space in recording the doings of the SOCIETY and it was quite evident from this and from the remarks of Mayor Hoan that chemistry has found an important place in the activities of the City of Milwaukee. Doubtless the recent meeting will help to impress its importance more firmly upon the public. This should be compensation, in a small way at least, for the splendid hospitality and untiring efforts of the Milwaukee Section in making the Sixty-sixth Meeting of the SOCIETY so successful.

University Photographic Laboratory

GUESTS OF WISCONSIN SECTION AT MADISON, WIS

The Council Meeting

Past Presidents Bancroft, Herty, Hillebrand, Smith, and Whitney, the officers of the SOCIETY, and 108 councilors were present at the council meeting which was held in Milwaukee on September 10.

The Prize Essay Contest was announced in some detail by the chairman of the committee, whose report was received with the enthusiasm due an undertaking of this importance.

Edgar F. Smith, chairman of the committee appointed after the Pittsburgh meeting to arrange all matters relative to the annual prize made possible by the Allied Chemical and Dye Corporation, reported that the committee had agreed upon "The American Chemical Prize" as the name of this annual award, and that the jury of award is to be a self-perpetuating body consisting of five representing the AMERICAN CHEMICAL SOCIETY and two appointed by the Allied Chemical and Dye Corporation. The Council not only approved the report as presented, but empowered its committee, consisting of Edgar F. Smith, C. F. Chandler, F. P. Venable, Ira Remsen, and Theodore W. Richards, to designate five who are officially to represent the SOCIETY upon the jury of award.

The application of the Section on Chemical Education to become a division was approved. A number of additional fellowships have been founded since our last annual meeting, and Secretary Parsons read a list of existing fellowships including these additions. This list will appear in the Proceedings.

Upon the motion of the Committee on the Metric System it was voted that hereafter the metric system should be used in all SOCIETY journal articles, with English equivalents in parenthesis if the authors so desire. The recent announcement that, following overtures by the drug manufacturers, the Public Health Service and later the Army had abandoned its former policy of purchasing drug and medical supplies by metric units on the plea of a slight economy, brought forth a resolution unanimously passed disapproving this action and expressing great disappointment at the step, which certainly appears to be a backward one.

The report of the editor of the *Technologic Monographs* was approved, as was the interim report of the Finance Committee, presented by the treasurer.

The invitation of the Washington Section to hold the spring meeting of 1924 in that city in April, with definite date to be announced later, was approved. The invitation of the Cornell Section to entertain the annual meeting in 1924 was unanimously accepted.

The Advisory Committee, having given careful consideration to the financial needs of the local sections, brought in a recommendation that beginning with 1924 local sections be given a rebate of $5.00 on each new member paying $15.00 dues, and $2.50 on any nonmember reinstated in membership after an interval of two years, provided this membership is originally transmitted to Secretary Parsons and rebate claimed by the secretary of the local section or the chairman of its membership committee.

It was voted that the Committee on Chemical Education of the Division of Chemical Education be made a committee of the Council.

When the Committee on Progress in Society Procedure reported at New Haven, its recommendation for the establishment of two special committees, one to investigate the question of intersectional or regional meetings and the other the classification of membership, was adopted. Both questions are complicated by a number of factors, and while the Council sees the wisdom of proceeding very slowly, there was some disappointment that circumstances made it impossible for more than progress reports to be made. One of the conditions has been the failure of many local sections to express their views on these questions. Both committees were continued and will endeavor to make reports at the Washington meeting, but no progress can be made by them unless those individuals and groups which have given thought to these matters express their views to the chairmen of the respective committees.

Both these committees having sprung from work before the Committee on Progress in Society Procedure, it occurred to several individual councilors that much time might have been gained had some member of the older committee been placed upon each of these new committees, so that some continuity in the work might have been maintained and the duplication of certain effort thereby avoided.

A new local section, with headquarters at State College, Pa., was authorized as soon as certain formal requirements have been met. The report of the Supervisory Committee on Standard Methods of Analysis was referred to the Advisory Committee and the motion to permit student members to become enrolled in September with dues of $3.50 for the balance of the year was approved. The editors were reëlected.

Another recommendation of the Council at New Haven creating an Executive Committee to replace the present Committee on National Policy, to have the usual powers of an executive committee and to have full authority to act ad interim for and in behalf of the Council on questions of national policy or import and to serve in an advisory capacity to the Council, was approved. This committee will consist of the immediate past president, the president, the secretary, the treasurer, the editors of the SOCIETY's journals, and three councilors. The present councilors, A. M. Comey and Wm. McPherson, were continued upon the new committee, and George D. Rosengarten was elected as a third member. The provision for the election of directors by some regional plan has been greatly desired by some sections, and a satisfactory plan having been devised by the Advisory Committee, this was unanimously adopted. It will require another year to put the plan into full effect. Full details will be given in the Proceedings.

The size of the Council then came under discussion and the recommendation of the Advisory Committee that the right to substitution be discontinued was refused. A number of other plans were suggested and debated at length, but the final action of the Council was that the size of the body is not to change. This is a reversal of the vote at New Haven.

The name of the Division of Leather Chemistry was changed to Leather and Gelatin Chemistry. There was prolonged discussion of two motions presented by the Leather Division. The first motion was intended to rescind the Council action that no papers be presented unless the titles are printed upon the final program. This motion was lost. The second motion was to bring about a modification of the action taken at Pittsburgh to the effect that nonmembers may not present papers before divisions and sections unless of unusual importance, and then only upon an agreement between the secretary of the division or section and of the SOCIETY. After prolonged debate the Council approved the action of the Secretary so far taken and instructed him to continue his present policy and interpretation, except as provided in an amendment to the Pittsburgh action—namely, "except papers invited by chairmen and secretaries of divisions, and that such papers are to be so designated on the program."

The Council approved the plan of encouraging the Cincinnati Section to organize an intersectional or regional meeting to be held in conjunction with that of Section C at the December, 1923, meeting of the American Society for the Advancement of Science.

While the discussion at times was spirited, the Council was harmonious to a degree. The actions taken were either unanimous or by considerable majorities, and there was both time and opportunity for extensive discussion and the relation of many experiences. After a hearty vote of thanks to all local officers and others contributing to an unusually successful meeting, adjournment was taken at 10:30 P.M.

The Market for Chemical Ideas[1]

By C. F. Burgess

C. F. Burgess Laboratories, Madison, Wis.

Were I to fall into the spirit of the times and try to emulate the big talkers of the day, I would dwell upon the noble work which chemists are doing in the cause of humanity; I would tell how they are being deprived by the big interests of their birthright—a living wage; I would show that they have no real market for their product, that Wall Street controls the situation; and I would urge that it is time for chemists to arise and throw off the shackles which are holding them in the ranks of the oppressed.

C. F. Burgess

But for various reasons, one of which is the scarcity of facts upon which to base such talk, I shall take an opposite course and even at the risk of incurring possible displeasure, I shall refer to the product of the chemists' brains, chemical ideas, as a commodity, and, therefore, subject to barter and exchange. I may find it necessary to depart from the time-honored custom of scientists and refer to the value of chemical ideas in terms of money, and I hope to be able to show that the chemist has in his own control the methods of regulating the returns for his services.

In using the term "chemist" in this discussion, I intend to refer only to those men of chemical training who have ability to do creative work, to produce "chemical ideas," as differentiating from the chemist who is confined to pure routine work, and is like the Ford type of mechanic, whose principal experience is "screwing in bolt No. 647." By the expression "chemical ideas" I refer to the discoveries, inventions, or proposals which are capable of being turned to the service of man through offering a new product, a new process, a "method of making two blades of grass grow where one grew before"—or, in other words, to those ideas which have a value, either immediate or potential.

During the past few years a great deal has been said about the earning power of research. Popular interest has been created. Graduate and undergraduate courses in chemistry show increased enrolment. There is a rapidly increasing volume of chemical literature and the production of chemical ideas is a growing industry. In chemical circles, however, the opinion prevails that the chemist is not sharing adequately in the profits which arise through the application of his ideas. Seldom is the suggestion made that there may be an over-production from chemical research and that the meager returns to the chemist are but a working out of the economic law of supply and demand.

In the sense that there is an established market for manufactured goods, for agricultural and mineral products, for the works of the writer and composer, it might be said that there is no organized or established market for chemical ideas. The producer of chemical ideas must do the best he can in a market which may at best be described as chaotic.

Such market as does exist may be classified into various divisions.

The one which furnishes the easiest path for marketing chemical ideas is that afforded by our scientific and technical societies, and by the publishers of scientific journals. To this the chemist brings his wares in the form of papers, monographs, or theses. There seems to be little restriction upon the volume which can be absorbed. The compensation secured through this outlet is indefinite and comes in a roundabout way. Through a peculiar system which has been evolved in our educational and other publicly endowed chemical laboratories, an investigator's advancement, title, and salary are determined in large measure by his research ability. And this in turn is often measured by the number of papers he has published. The public, which supports these laboratories, is in the end the actual purchaser of these papers, and buys at low prices. Knowing something of the salaries of college research men, and of the amounts which constitute an increase of salary, I would not estimate the selling price to be more than a few hundred dollars per paper.

This market has the advantage of size, and the disadvantage of offering small returns to the producer. It can be criticized from the standpoint of the public. Some weeks ago I participated in a discussion at a meeting of the directors of a national scientific society, the debated question being the increasing mediocrity in the quality of chemical papers finding their way into the chemical journals. The opinion prevailed that the system of forcing laboratory workers to write numerous papers, often presenting fragmentary investigations coupled with a lack of proper censorship as to quality, is a factor contributing to an unfortunate deterioration in current chemical literature. In other words, this market is likely to be disrupted unless attention is given to improving the quality of goods dumped upon it.

The second division of the market for chemical ideas is that in which the chemist contracts to furnish his entire supply to his employer, usually one engaged in the business of manufacturing. The market price is embodied in the salary under which the chemist accepts employment. Many a worker finds this is an unsatisfactory market in which to deal, because it involves sacrifice of independence and an exclusion of other outlets for his discoveries. He feels that this loss is not compensated fully by the amount of salary paid. He may see his ideas adopted freely by the management. Presumably, the corporation prospers, but without giving the chemist the compensation which he considers his due.

When the chemist looks for larger financial return than is afforded through publication, and is unwilling to sacrifice his independence by accepting a salary, he has recourse to a third division of markets, which is open to him if he can show property rights or title to his discovery or invention. This he can do by establishing it as a trade secret, or making it the subject of a United States patent. It is beyond the scope of this paper to discuss trade secrets or patents, but it is certainly not outside the essential duties of the chemist to familiarize himself with the law relating to trade secrets, and the complex details of the patent art, if he ventures into this field of marketing.

Perhaps the chemist who presents his ideas to an unappreciative world may profit by the words of the noted divine who said:

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[1] Title on program, "Marketing Chemical Discoveries."

"When I find an audience cold and unresponsive, I do not seek consolation in blaming the audience. I know there is something lacking in myself and I seek to remedy my defects."

Let us, therefore, look at the position of the chemist from the viewpoint of the public and through the eyes of the business executive who has to deal with research as an adjunct to industry.

From this viewpoint there is no tendency to belittle the importance of chemical research; the fundamental value of chemical ideas is recognized universally; in the distance can be seen new industrial worlds to be conquered through the chemist's leadership. The store house of chemical knowledge to which he is continually adding has become an immensely valuable asset to industry.

But attention must be called to the fact that just as a manufacturer's inventory of raw material may be larger than is necessary for the current needs of a business and thus become a dead rather than a live asset, so the store house of chemical knowledge can be overcrowded with ideas at a rate greater than that at which they can be put to practical use.

This is a condition which must be recognized. It has been estimated that if all chemical research work were discontinued for twenty years, industry would still progress through reduction to practice of the many chemical ideas which have been offered in the past. The lapse of time, sometimes short but usually long, between the chemical discovery and its reduction to commercial practice accounts in part for our large inventory of chemical knowledge, and for the manufacturer's inability to pay large prices for new ideas which cannot be used at once.

To apply an idea may upset a long-established routine carried out by trained workers, involving the upbuilding of a new organization; the discovery of a new and better raw material may mean the abandonment of a plant in one place and its reëstablishment elsewhere; another proposal may have to await the whims of a legislature. Delays such as these may tax the patience of the chemist.

The business man has been criticized for his lack of chemical knowledge, and his consequent indifference to or ignorance of the work the chemist is doing. But it is asking the impossible to expect the busy executive to review and pass judgment on the value of chemical ideas as rapidly as they are presented. In every plant where chemists are employed new ideas and proposals are coming up continually. As a fair index to the number of chemical ideas being offered to the public, the abstracts of the AMERICAN CHEMICAL SOCIETY may be cited. Assuming that each abstract refers to an idea embodied in some book, paper, pamphlet, or patent, the current monthly volumes show that a new chemical idea is presented to the public at the rate of one for every five minutes of the business day.

The immensity of the volume of chemical literature through which the business man struggles in his endeavor to keep abreast of chemical knowledge is bad enough, but the task is made more difficult by the chemist's language, a language of words, formulas, and symbols which mean no more to the uninitiated than the cryptic, mystical expressions of the medieval alchemist do to the modern worker. The truth of this statement can be tested by choosing almost any paper presented before this SOCIETY, and asking some intelligent banker or other type of business man—possessing an academic degree, if you wish—to read the paper and tell what he finds in it. The chances are that he will laugh.

To the complaint that business is blind to the opportunities for profit which the adoption of new chemical ideas affords, the reply is that if the chemist has something meritorious to sell it is necessary for him to practice "the science of human service" (business), which embraces the art of imparting knowledge to the public (advertising).

It is a notorious fact that chemists are deficient in the science of salesmanship; their writings fail by far from "touching the imagination of crowds." I have asked various investigators why they confine their announcements of discoveries to the scientific journals and do not reveal them to the larger public through the daily press. Their attitude may be typified by the following questions and answers of a conversation held some months ago with an active and honored member of this SOCIETY.

If you are disappointed in the interest shown in your recent discoveries, why do you not try an announcement through the Associated Press?

That is out of the question. My principal concern is to see that the daily papers do *not* attempt to describe my work. I have been terribly embarrassed by the garbled reports which have been given out concerning some of my discoveries.

Why do you not prepare, then, an accurate statement in newspaper style? If the subject matter is of importance and written clearly so as to be understandable, your contributions will be welcomed.

You are suggesting the impossible, for an adequate description cannot be written without using scientific terms and formulas, which are, of course, unintelligible to the newspaper reader.

That man failed to appreciate the well-known truth that no man can become complete master of his subject without being able to explain it in a manner intelligible to the average man.

The exceptional view was held by another member of this Society. He has contributed many papers, and could tell you, if he would, that a public press announcement of a certain discovery brought him a hundredfold greater correspondence with interested persons than he had ever had from a paper published in the chemical journals. In other words, as an advertising medium the daily press has a far greater drawing power than has the scientific journal.

While the average chemist finds it impossible to write his own advertisement, there are notable examples of ability in this field. Dr. Robert Kennedy Duncan has shown how the chemical idea can be sold to the public, and although he incurred the displeasure of fellow chemists in his use of popular language, he rendered a monumental service to the downtrodden chemist.

If the popular appeal does not fit in with his standards of ethics and professional pride, the chemist must admit that Pasteur lost nothing in dignity or professional standing when he uttered that forceful appeal which might well be placed among the classics in advertising:

> I have a head full of the most beautiful projects for work. I am ready for new productions. Oh, why am I not rich—a millionaire? I would say to you: Come, we shall transform the world by our discoveries.

The business executive will admit that the salaries of chemical workers are low and that few chemists advance into the better paid administrative and executive positions. But he will deny that there is any system working against the chemist's advancement other than the chemist's own inability or lack of interest in handling the business problems that are always involved in the reduction to practice of a chemical idea.

One employer says that his greatest difficulty with his chemical workers is their tendency to study their equities in the business without showing a willingness to follow the chemical idea from the laboratory through the semicommercial stage and into full commercial operation, or dealing helpfully with all the problems of equipment design, handling of labor, marketing difficulties, and the like.

It is the experience of employers that it takes time for the chemistry graduate to go through the disillusionment period before he can become a valuable coöperating force in the business organization; the longer he has been trained in academic work the harder it is for him to become adjusted to industrial conditions. During a discussion of this feature before a branch meeting of this Society, the executive officer of one of the largest industrial laboratories said that his company had compiled a rating of the universities on the basis of time taken for graduates to adapt themselves to industrial research and development. Under this rating the range is from four years for some of the larger universities to one year for certain of the smaller. This is mentioned as being suggestive of the help which the educational institutions might give in increasing the service value of their graduates.

From the management standpoint much study has been given the question of adequate compensation to the chemical worker, just as it has been given to other classes of producers; but the chemical idea is such an intangible commodity that its valuation is exceedingly difficult. As an illustration I recall the solution of a problem for increasing the production of a certain manufactured article.

The standard rate of production was 800 per day per employee. The chemist proposed a quick drying adhesive as a means of increased yield, and he showed how the output figure could be increased to 1200. One of the shop workers then made a time study of the operator's movements, redesigned the work tables, and installed a conveyor system, resulting in an increase to 2000, and the shop superintendent, by installing a carefully worked-out piece rate and bonus system, succeeded in increasing the production to about 5000 units per day. It required over a year to effect these improvements and of this time the chemist contributed perhaps two or three days in the beginning of the period.

To value the equities in the final result becomes much like crediting to the little acorn its property right in the tall oak. If the chemist had exercised the opportunity presented to him he could have supplemented his chemical study with suggestions as to management and payment of labor. His contribution to the business success would have been more easy of calculation, and his opportunity for advancement into increased responsibility would have been bettered.

The average chemist is so little posted on patent matters that he shares the general popular misconception of the actual value of a patent. Even though a patent may be secured with little more expense than is involved in the purchase of a good suit of clothes, the newspapers in the home town have a practice of announcing as of news interest the awarding of a patent to one of its local inventors, and as the inventor passes down Main Street he is stopped by his fellow citizens, who congratulate him upon his good fortune.

When he offers his patent to the business executive he is greeted in a far different manner. He is asked whether the patent has been validated by the courts. The cautious investor knows that if a patent happens to be of little value its validity will never be questioned, but that if it is of importance infringement is sure to follow. If the infringers are to be prosecuted, litigation with its attendant expense results. This may necessitate an investment of a few thousand dollars, or a few hundred thousand dollars. Another question raised by the purchaser is this: Will the patent give the right of use without infringing the rights of others? This question is answered in the form of an opinion by the legal department which must first institute a search through all the patent literature as well as other publications. Such a search usually involves an investment of over one thousand dollars, and I have known of validity searches costing over fifty times that figure.

If the inventor is willing to share the labor and expense of conducting these investigations and litigations and coöperate in working out the ideas to a commercial success, he becomes a business man and as such can deal on much better terms in securing his rewards than he can if he wishes to turn over his patented invention without assuming responsibilities.

We may wonder why the chemist holds himself aloof from business affairs. Perhaps his pride and dignity stand in his way. In a suggested code of ethics for chemists, published recently, appears this clause:

> The chemist should not use his professional standing as a means of sponsoring or promoting commercial or other undertakings of a speculative character.

From the numerous hazards surrounding a manufacturing undertaking we know that it cannot help but be speculative in character. Even the railroad business has become so speculative that few will invest in its stock. If the chemist puts himself on a pedestal and refuses his whole-hearted support to an enterprise in which he may believe but which is nevertheless speculative, he places himself outside of a coöperative relationship with the man of business.

In a bitter tirade against existing conditions, entitled "Is a Commercial War between Chemists and Business Men Coming?,"[2] the threat is made that if the interests do not better recognize the chemist's work, there will be an uprising in which chemists will become business men and as such will receive the rewards to which they are entitled. Far from throwing fear into the commercial world the carrying out of this threat would be welcomed by employers who complain that chemists take too little interest in business affairs.

Perhaps a useful step in this direction is being taken by some of our universities in combining business courses with courses in chemistry; but the greatest opportunity lies in encouraging research men who have already received their degrees to take a greater interest and share in working out business problems. Just how this can be done remains for the individual worker to decide.

To the man trained in academic research who contemplates the establishment of a business enterprise, a word and, in fact, several words of caution may be offered. He will find the various state legislatures pass 26,000 or more laws every two years and that many of these involve compliance on his part. He will find that the laxity in ventilating facilities, appliances for safety, and methods of fire prevention found in university laboratories is not permitted in industrial plants. Inspectors of various kinds clothed with governmental authority will call upon him at frequent intervals to tell him just what he must and must not do. Commercial credit houses will ask him to furnish a detailed financial report and proofs that he is willing and able to pay his debts. No matter what his own confidence may be in the success of his undertaking, his banker will tell him that he considers him a purely speculative risk and must continue to do so until he has established a seasoned industry with demonstrated ability to pay dividends over a period of years.

The opportunities for getting into litigation are boundless, and legal expenses become an unavoidable part of his overhead expense. The blue sky department may try to prove he is less prosperous than he thinks he is and the income tax auditors may assert that he is more prosperous than he claims to be. If incidents such as these can be met by the chemist as patiently and cheerfully as he meets the problems involved in laboratory research, the chances for pleasure and profit from his business are excellent.

As bearing upon the opportunities for success in carrying on research as a business venture, I am privileged to describe an experiment which was begun thirteen years ago and is still under way. A small group of men trained in chemical research joined in the organization of a corporation under the laws of the State of Wisconsin, with the purpose of carrying on investigations of the kind which abound in college laboratories. The resulting discoveries were to be marketed as patent rights, trade secrets, as a part of consulting service, or as a manufactured product in which the results of research were to be incorporated.

One of the incorporators had served fifteen years in educational work and in laboratory research along chemical and electrochemical lines. One had ten years' record of both university and industrial laboratory work in chemistry and chemical engineering; another had served for eight years as chemist in an industrial laboratory; another presented ten years' experience in commercial foundry practice and two years in college research. A fifth man had just completed his university training. A practicing attorney constituted the sixth member of the group that conducted the business during the early years.

The thirteen years' record of this organization is an interesting story, ludicrous in some spots, and bordering on the tragic in others. Many chemical ideas were evolved, and all the ways of marketing hitherto referred to were tried out. Many of the undertakings failed, and some of them succeeded. Licenses have been granted on some of the ideas, other ideas have been sold, still others have been made the basis of manufacturing business controlled by the laboratory corporation.

Whether the experiment as a whole is a success may be a matter of opinion. To form the basis of such opinion I may give some facts. The original capital was $9000. This has been increased through earnings and sale of stock to over $900,000. The annual sales of ideas and of material products have increased to $3,000,000, and with a world-wide distribution. Manufactured products of others and employing the discoveries of the laboratories run into much larger figures. Two industries manufacturing new products have been created and several other similar projects are now under way. The personnel has naturally increased greatly in numbers to a total of over six hundred men and women. At the present time twelve of these are men trained in science and engineering, most of whom occupy executive positions or are actively engaged in directing productive work.

What about the rewards which come to the individual workers? As to how their financial returns compare with those received in other fields, I am unable to say, but there is abundant evidence to show that inspiration and joy come in prosecuting research under conditions in which the worker can watch his idea, started in the laboratory, becoming an instrument of service to mankind.

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[1] *Chem. Age*, **31**, 255 (1923).

[2] THIS JOURNAL, **14**, 356 (1922).

Bacteria and the Chemist

By Arthur Isaac Kendall

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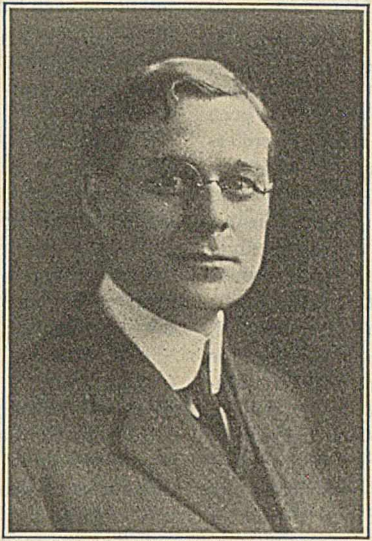
IT IS distinctive of the fundamental sciences that as their respective fields of inquiry become more completely explored, frontiers which in earlier periods of their development appeared to limit their scope, imperceptibly merge with those of related or coextensive subjects. This tendency toward amplification is peculiarly noticeable in the history of chemistry. In the earlier days, before complex compounds of carbon were well studied, the phenomena of life processes and the environmental interchanges associated therewith were presumed to be endowed with an intangible "vital principle," wholly unapproachable from the investigative side. With the rise and development of organic chemistry, however, and particularly after the synthesis of urea—an important waste product inseparably associated with higher animal life—from ammonia and lead cyanate by Wöhler (1828), the vitalistic conception of life began to give way. The belief is rapidly gaining ground that the dynamics of life itself may be expressible in terms of chemical equations; indeed, some of the simpler of these equations are already qualitatively understood. At the present time, of all the fundamental sciences, biological chemistry, "the handmaiden of medicine," is justly regarded as holding forth the greatest promise of fruitful contributions to the interpretation of the mysteries of these vital processes.



A. I. Kendall

Life appears to be essentially a continuous interchange between an organism and its environment. Death intervenes when this interchange ceases. The investigation of the nature of this interchange lies within the domain of chemistry. In organisms of great structural differentiation, as animals and man, the association of many simultaneous reactions, inevitable from the cellular division of labor, masks the elemental phenomena of the chemical interchange which continually takes place between the organism and its environment. It seems justifiable, therefore, to turn to simpler living entities than man or animals for the unfolding of the chemical pattern upon which the more complex reactions are molded.

Among the simplest of known living things are the bacteria, that group of asexual, unicellular organisms found at the very foot of the ladder of life. All the fundamental phenomena and manifestations of life—morphology, hereditary architecture, nutrition, and reproduction—are performed in this group by units so minute that fully fifteen millions of million of them would scarcely balance an ounce weight. The ratio of surface exposure to volume, furthermore, a factor which determines in a very large degree the magnitude of their energy requirements, is relatively great.

Finally, reproduction is, or may be, extremely rapid among the bacteria. In the more vigorously growing types, as for example the cholera microbe, that dread germ which incites Asiatic cholera, successive generations of fully mature organisms may appear at intervals as frequent as every fifteen minutes. In as much as there are ninety-six periods of fifteen minutes' duration in one day, the theoretical descendants of this germ would be 2^{96} in twenty-four hours. This is indeed a truly prodigious number; fortunately, it never is and never can be even approximated. Nature interposes insuperable barriers to such a theoretical progeny, but even with the limitations of diminishing food supply, accumulation of waste products, and other environmental deterrents, the spawn of a single microbe number countless millions within a very short time.

These facts, together with the comparative readiness with which pure cultures may be procured and kept alive, make the bacteria peculiarly adapted to the study of the chemical phenomena of life reduced to its lowest terms. Such studies as have been made of the nature of the chemistry of bacterial interchange with their nutritive environment—their metabolism, as it is properly designated—have revealed an unexpected similarity with the general phenomena of metabolism in higher organisms, as animals and man. Perhaps this might have been anticipated.

Bacteria are fundamentally digestive systems, and they are endowed with the power of deriving the energy essential for their life processes from chemical substances of varied, but by no means unlimited, composition and stereo-configuration. Each kind of microbe, indeed, exhibits striking fastidiousness in its choice of these energy-containing substances. Herein lies a most important relationship between the microbe and the chemist. A word in explanation will make this point clear.

There are two important phases clearly discernible in the life history of bacteria—a structural phase, in which the microbe reproduces and transmits to its progeny the hereditary chemical architecture characteristic of its kind; and an energy phase, in which the mature microbe and its descendants perform their characteristic functions, or chemical transformations of their nutritive environment.

In point of time the structural phase precedes the energy phase. In the amount of chemical interchange, the energy phase exceeds the structural phase many fold. Also—and this is important—the general characters of the chemistry of structural development and that of the energy interchange are quite unlike. The former is inseparably associated with the proteinization of nitrogen; the latter is inextricably bound up with the oxidization of carbon.

Stated differently, nitrogen is as essential for the structure of the bacterial cell as iron is for the structure of a locomotive; and carbon is as necessary for the energy requirements of the bacterial cell as coal is for the moving of the locomotive. The amounts of chemical substance required, respectively, for the structural and energy phases of bacterial development also are very unequal, even as the weights of iron and of coal are unequal in the respective structural and energy phases in the life history of the locomotive.

A suitable medium frequently used for the cultivation of most bacteria is prepared from a clear watery infusion of meat, reinforced with peptone. This is ordinarily referred to as plain nutrient broth, or plain broth. It contains salts, including phosphates, water, and complex compounds of nitrogen, carbon, hydrogen, and oxygen. The latter are complexes of the amino acids, of which about nineteen are well known. These in various combinations confer upon proteins their specificity. In such a medium most bacteria find all the nitrogenous constituents for their structural needs and also the carbon necessary for their energy requirements.

Bacteria could not grow if nitrogen in proper combination were not available; hence, this plain broth, which offers to bacteria the requisite nitrogenous constituents, is the nutritive basis for ordinary microbic cultivation.

The carbon of amino acids and of peptone is not so readily utilized for energy, however, as the carbon of carbohydrates; consequently, it is frequently advantageous to add some glucose or lactose, or other member of the carbohydrate group, to the plain broth. In such a glucose broth or lactose broth medium, the microbes clearly have a choice between the carbon of the amino acids and the carbon of the carbohydrates for their energy requirements. If the stereo-configuration of the protoplasm—that is, the living substance—of the microbe fits the stereo-configuration of the glucose, or the lactose, or whatever carbohydrate has been added, the microbe will turn to the sugar for its energy in preference to the amino acid, utilizing the amino nitrogen of the latter, of course, both for its own structural needs and the structural needs of its progeny. In physiological parlance, the utilizable carbohydrate spares the protein constituents of the medium from bacterial decomposition, aside from the very small amount of the latter required to build up the bodies of the microbes.

It is not a matter of indifference which type of compound, carbohydrate or amino acid, is used by the various microbes for energy. Thus, diphtheria bacilli grown in plain broth, containing no carbohydrate, produce that extremely potent soluble poison or toxin known as diphtheria toxin, which constitutes the aggressive weapon of this formidable germ. If, however, a small amount of glucose is added to plain broth before the diphtheria bacillus develops in it, the resulting growth product is radically different. It no longer contains the potent poison; in place of this powerful toxin the culture medium contains lactic acid, the chemical basis of buttermilk.

Here is in actuality the realization of that strange conception of Dr. Jekyll and Mr. Hyde, which Robert Louis Stevenson has made so well known. The plot is unique. The same individual, under the influence of a chemical, changes his disposition from that of a useful member of society to that of a miscreant. The difference between diphtheria poison and buttermilk is surely as great a divergence in activity as that of the dual personality of the fabulous Dr. Jekyll and Mr. Hyde.

The striking change brought about by the addition of utilizable carbohydrate to a plain broth inoculum of the diphtheria bacillus is but one of a large number of examples well known among the bacteria, however, and its significance is far deeper than a mere actual living instance of a hitherto pleasant myth.

In the field of medicine, for example, the baneful effects of typhoid, cholera, dysentery, and other germs that cause severe infections in the alimentary canal can be ameliorated through proper dietary procedures, and the character of their products can be changed from poisons to lactic acid by the same measures that reformed, as it were, the activities of the diphtheria bacillus in culture media. This procedure of dietary therapy has been practiced successfully in typhoid and dysentery.

For the chemist, however, the underlying principle of the influence of carbohydrates upon the character of microbic chemistry has a very practical bearing. Space does not permit of a discussion of the possibilities in this field except in a relatively restricted group of substances, the carbohydrates. Inasmuch as carbohydrates are of great interest and importance both in animal and human nutrition and in many industries, however, this limitation is not incompatible with a survey of the relations of the microbe to the chemist.

Returning to the diphtheria bacillus, it will be recalled that in a plain, glucose-free medium, a potent specific toxin is produced. Also, the reaction of the medium becomes progressively more alkaline. In the same medium to which glucose is added—that is to say, in glucose broth—there is no toxin formed and the reaction becomes progressively acid, owing to the formation of lactic acid.

Herein lies a chemical test for glucose. Either the absence of toxin or the increase in acidity would with suitable controls be diagnostic. Extending this type of test to a library of microbes, each of which possesses the power of fermenting or utilizing certain definite carbohydrate configurations, there is at once available a new method of detecting and identifying members of the carbohydrate group.

Several methods of procedure follow from this utilization of microbes as chemical reagents. First, the identification of an unknown member of the sugar group. This is readily accomplished through a series of bacteria, each of which will use only certain sugar configurations.

Secondly, the recognition of impurities in carbohydrate samples.

Thirdly, the quantitative estimation of carbohydrates, both singly and in mixture.

Fourthly, the identification of hydrolytic products resulting from the cleavage of complex carbohydrates.

These various procedures have been used successfully in a limited group of sugars, and the entire carbohydrate group is open to exploration by this comparatively simple method of microbic analysis.

It is of some interest to know how sensitive the bacterial reagent is—how small an amount of sugar can be definitely detected. A long series of experiments has shown that as little as one one-thousandth of a per cent, or one one-hundred-thousandth of a gram, of a utilizable carbohydrate dissolved in a cubic centimeter of a culture medium may, under favorable conditions, give definite indication of its presence.

When one realizes that two unlike sugars, as glucose and lactose, may have nearly the same optical rotation and about the same reducing power, it will be seen that the microbe holds forth possibilities of interest and importance in this field.

In the animal and human bodies, several problems are still unsolved which would seem to be approachable from the standpoint of the microbe chemist—the place of formation of lactose in the lactating animal; the differentiation between glucose, pentoses, lactose, and glycuronic acid in the urine; the identification of the sugars which are found in the nucleins and in the brain, and also the stereo-configuration of the sugar in the blood and the tissues.

The direct relationship between glucose, the sugar of the blood and tissues in the human body, and the energy derived therefrom focuses attention upon the corresponding phenomena in bacteria. The stereo-configuration of the protoplasm of the living cell and its ability to utilize a similar, compatible sugar configuration seems to be one of the fundamental reactions of life itself. The intimate workings of this energy complex yet remain to be unfolded, and the answer must be sought for in the domain of chemistry.

Finally, a word about bacteria in the industries. Some of the most venerable processes known to mankind depend upon microbic participation. The retting of flax in the manufacture of linen, the tanning of leather, various fermentation processes associated with the souring of milk, sauerkraut, ensilage, the manufacture of vinegar, and various alcohols, as butyl, and ethyl alcohol, acetone, glycerol, and even the initial steps in the manufacture of synthetic rubber, are but a few instances of the deliberate exploitation or spontaneous activity of microbes.

As time goes on and knowledge becomes more complete, the chemist will utilize this cheap, ceaseless energy of the microbe to perform almost numberless processes that are unattainable at present or accomplished only by an extortionate expenditure of energy.

NINTH NATIONAL EXPOSITION OF CHEMICAL INDUSTRIES

UPON entering the Ninth National Exposition of Chemical Industries held at the Grand Central Palace, New York, September 17 to 22, one's first impression was that the entire scheme of things had been arranged with taste and a keen eye to a general pleasing effect. At the extreme end of the center aisle hung a large placard bearing this legend:

> **CHEMISTRY IS THE PRIMARY ELEMENT THAT GOVERNS SUCCESSFUL MANUFACTURING**
>
> If the chemical and chemical equipment industries represented at the Exposition should cease operating for one year, every vital industry of the United States might be forced to suspend operations before the expiration of that period.—*Rubber Age.*

The most casual visitor could not fail to be impressed with the fact that the chemical industries play an increasingly large part in the world's work. Former expositions were not so well balanced as the one of this year; the individual exhibits showed greater thoughtfulness on the part of exhibitors and concentration upon a few products or pieces of apparatus, which were thereby made more interesting and intelligible to the visitor. Fewer booths contained the conventional lounging chairs and settees, and there was a tendency on the part of all exhibitors to add something of educational value to the exposition and to avoid merely filling their space with miscellaneous collections of unrelated material. As a result more real information was available than on previous occasions; definite ideas definitely presented were met everywhere.

Undoubtedly, the exhibitors are profiting by the experience of previous expositions, and, following the agitation of last year for a different type of exposition under a different management, it appears certain that the management of the National Exposition of Chemical Industries has made an effort to meet some of the criticisms. The enlarged advisory committee, upon which all the elements of the industry are now represented, has had a more deciding voice in the proceedings than heretofore. The results speak for themselves. From year to year the exposition has contained fewer representatives of the actual manufacturers of chemicals and an increasing number of those who have something to sell to the chemical industry. Chemists generally look upon this as undesirable, for, if continued, this policy would result in an exposition of those who are purveyors to chemistry rather than one which demonstrates the progress of chemistry in America. This fault has been overcome to some extent by the equipment of booths to illustrate the progress of special branches of the chemical industry, rather than the products of individual manufacturers.

A notable example of this was the booth devoted to American dyes, where the contention that "American Dyes Are Fast" was clearly demonstrated through the coöperation of manufacturers of dyes and textiles and laundrymen, ably assisted by a manufacturer of dress patterns and attractive living models. The exhibits devoted to insulin and intarvin, the year's outstanding chemical contributions to the treatment of diabetes, to chemistry in the service of radio, to the Chemical Warfare Service, to the Bureau of Standards, and the illustrations of the earning power of research presented by the American Chemical Society, all present new developments in the service of chemistry to civilization and show to what extent exhibits interesting to both the chemist and the public may be made a part of the exposition. The demonstration of such new developments is believed to be more effective than the use of booths to display numbers of specimen bottles filled with materials already familiar to those who visit the exposition.

The experience of certain groups of chemical engineering students in utilizing the opportunities for instruction afforded by the exposition led to the initiation of a new policy at the Ninth Exposition. Before the summer vacation professors were invited to enrol members of their classes, particularly juniors in chemical engineering, in a Students' Course on the Fundamentals of Chemical Engineering and Industrial Chemical Practice. Of those who registered about 125 took the course, which had the following major topics:

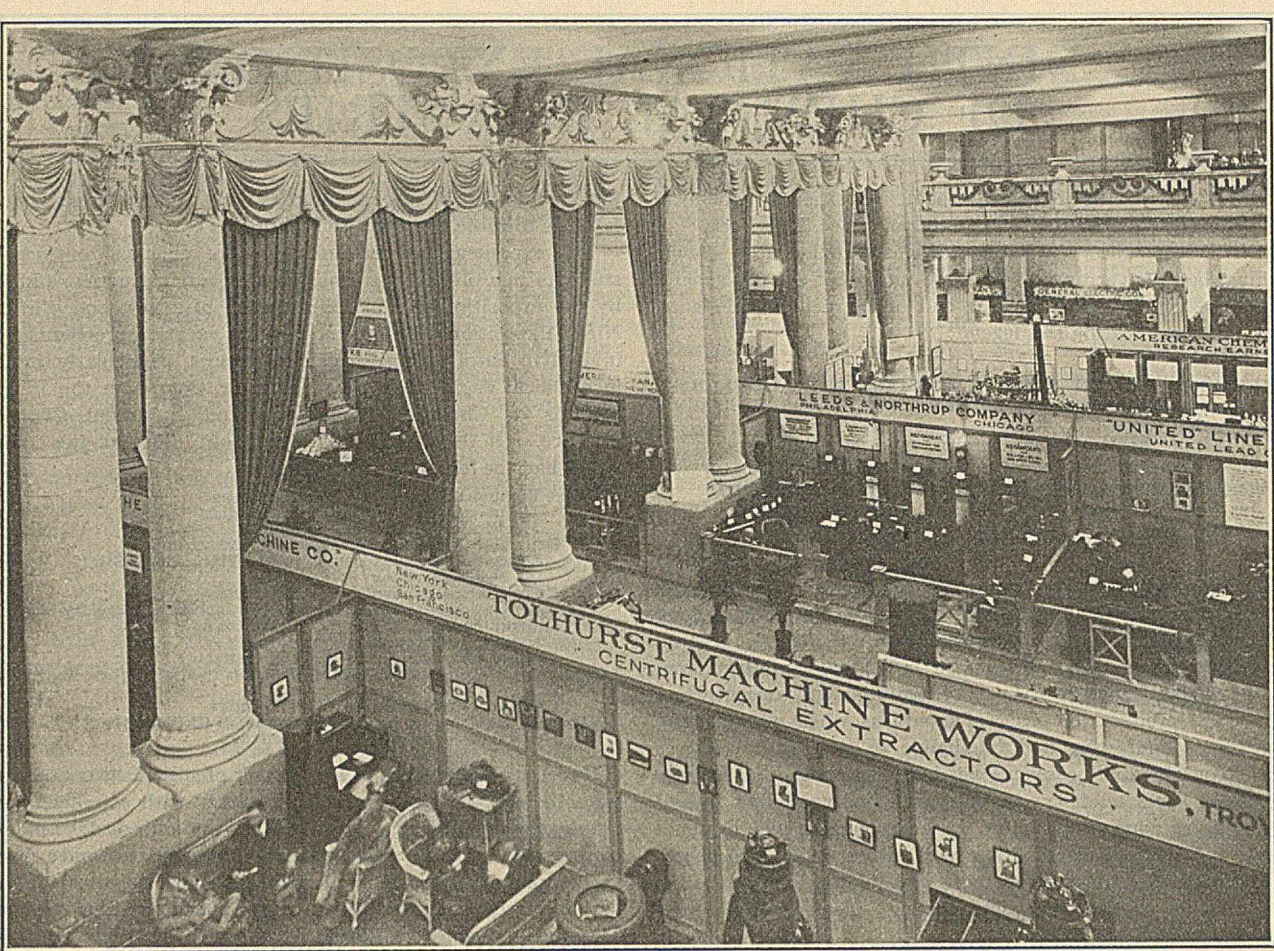
1—Plant Equipment in the Chemical Industries
    (*a*) Disintegration—Crushing and Grinding
    (*b*) Mechanical Separation—Grading
      General discussion led by Galen H. Clevenger
    (*c*) Separation of Solids from Liquids—Thickening, Filtration, Centrifugal Separation
      General discussion led by H. N. Spicer
    (*d*) Separation with Phase Change—Evaporation, Distillation, Drying
      General discussion led by W. H. McAdams
    (*e*) Handling of Materials
      General discussion led by A. E. Marshall
2—Materials of Construction, What Materials to Use: When, Where, and Why
      General discussion led by W. S. Calcott
3—Chemicals in Commerce, the Distribution of Chemicals
      General discussion led by E. V. Peters

Under each of these topics a number of specialists contributed from their experience, and this, together with afternoons and evenings spent in the studies of exhibits and of industrial motion pictures, led up to a general review, various quizzes, and a checking of reports. To facilitate the arrangement of the course Columbia University generously arranged for housing visiting students. The students' course satisfactorily replaced the special addresses heretofore included in the program of the exposition. Each afternoon and evening special programs of motion pictures were offered, these being industrial in character and especially informing.

With this year the plan of the exposition is to be changed to biennial. This should result in an increase in the number of exhibits, the ease with which they are planned, and the interest which they carry when the Tenth Exposition is opened. The chemical manufacturers themselves must not fail in their support of the enterprise, since it is directly in their interest to assist in thus bringing to the public a clearer understanding of what the chemical industry as a whole means to it. The view held by some that the only people exhibitors care to have call at their booths are those in position to leave an order, we believe to be narrow, for, while few of the exhibitors cater directly to the public through retail channels, yet ultimately all the products of the industry are consumed by individuals whose interest should be secured and held. Very few of the questions asked by the visiting public are unintelligent, and the effort made this year to have exhibits clearly understood seems to be an argument against discouraging the attendance of the general public.

The management deserves much credit for the wide publicity given the exposition. The attendance of a large number of business men is due to its efforts. To describe the individual exhibits would require more space than is available here, but if the number of exhibitors was less than last year, there is no doubt but that the interest of the visitor was more securely held than on previous occasions. The chemists are grateful for the support given the enterprise, and the American Chemical Society acknowledges with appreciation those laboratories which contributed examples of their work to prove that research does earn dividends.

All in all the Ninth Exposition showed a marked improvement over the Eighth and may be taken as an indication that the one two years hence will be the best of its kind yet conceived.



American Chemical Society Exhibit

It is the privilege of THIS JOURNAL to publish from time to time references to the earning power of research, and in line with this policy there were shown at the booth of the SOCIETY a few concrete examples of research as a factor in earning dividends. Materials displayed were contributed by the Industrial Fibre Company, the National Lamp Works of the General Electric Company, the Geophysical Laboratory of the Carnegie Institution of Washington, the Union Carbide & Carbon Research Corporation, the General Electric Company, the Ward Baking Company, the Union Pacific System, Arthur D. Little, Inc., and the Miner Laboratories. The materials, arranged in units, were made self-explanatory by large placards, the wording of which is quoted below:

RESEARCH IN GROWING SUGAR

Wastes utilized to prevent other wastes is often the result of research. Ten tons more cane per acre (equivalent to one ton raw sugar) and 50 to 70 per cent less labor in the field followed the use of a paper made from waste cane bagasse in the cane fields of Hawaii to prevent the growth of weeds.

RESEARCH ON WATER SUPPLY

The life of locomotive boilers has been lengthened sevenfold and the coal consumed in operation reduced by many millions of tons per year through the application of research to water supply on our railroads. The life of a locomotive fire box (costing $1700) on a certain bad water was two years. After treating the water properly to prevent corrosion, the steel lasted fourteen years, making a saving of more than $700 per locomotive per year.

RESEARCH IN BREAD MAKING

Two outstanding examples of the value of research to the baking industry:

(1) A food for yeast, consisting of a mixture of mineral salts, prevents a yearly waste in the fermentation process of 200,000 barrels of flour, 30,000 barrels of sugar, and 15,000,000 pounds of yeast. These savings reach the amazing total of $5,000,000 yearly.

(2) A loaf of white bread which contains within itself all the elements necessary for a complete diet. The composition to this bread and the comparative feeding experiments on animals are shown. Experiments on human subjects have not yet been completed.

RESEARCH AND X-RAYS

The modern efficient X-ray tube is distinctly a product of research, and is becoming more and more a tool for further research. Its uses in treating disease, in watching the functions of the vital organs in the human body, and in detecting foreign substances in living and inanimate bodies are well known. The use of X-rays in determining the constitution of matter (space arrangement of atoms in the molecules) is still in its infancy, but results already achieved indicate that future accomplishments in this field will be of extreme importance in the solution of this problem.

RESEARCH IN ELECTRIC LIGHTING

Organized and continuous research on the lighting problem has produced types of lamps with which this country's lighting bill in 1922 was one and a half billion dollars less than the cost of the same amount of light if the best lamps available less than 20 years ago had been used. This represents a saving, among other things, of 25,000,000 tons of coal.

RESEARCH ON WASTE MATERIAL

The value of oat hulls is increased 800 per cent by conversion into furfural, the cheapest commercial aldehyde, having many industrial uses. Thus through research a waste becomes a raw material for a new industry.

RESEARCH AND ARTIFICIAL SILK

Through research, wood pulp and other cellulose materials valued at approximately five cents per pound are converted into artificial silk, valued at an average of $2.50 per pound. The value of the artificial silk produced in the United States is approximately forty-five million dollars per year.

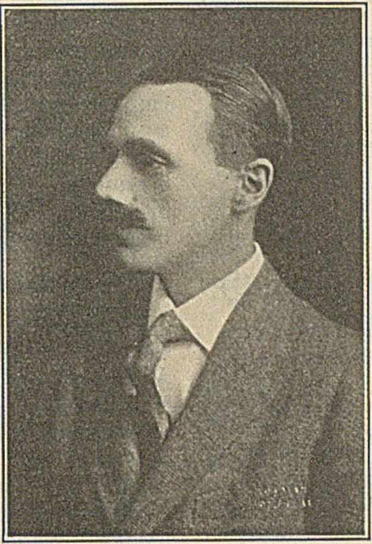
This exhibit shows viscose silk made from wood pulp.

Accelerators of Vulcanization

By G. Stafford Whitby

McGill University, Montreal, Canada

HAD it not been that the mixture employed contained a catalyst, Goodyear might not have discovered the peculiar effect of heating rubber with sulfur, now known as vulcanization, which involves such an important change in the physical properties of rubber that it is the basis of the present-day rubber manufacturing industry. The catalyst used by Goodyear was an inorganic lead compound, and inorganic catalysts, particularly oxides of lead, calcium, and magnesium, have been continuously and largely used by the rubber industry, although it is only recently that an explanation of their mode of action[1] has seemed possible.



G. Stafford Whitby

Within the last decade it has been found that many organic compounds act as accelerators of vulcanization, and a number of such compounds have come into wide technical use. Organic accelerators have proved to possess capabilities so much wider and more valuable than those of inorganic accelerators, that they have attracted much more study than has been given to the latter. Furthermore at the time their existence was discovered, rubber manufacturing, which had previously been conducted on almost entirely empirical lines, began to be an object of scientific study.

To designate an agent which when present in a small proportion hastens the rate of vulcanization of rubber, the term "accelerator" is preferred to "catalyst," because it is believed that, in some cases at least, not the agent originally introduced into the rubber, but a product derived from it by decomposition or reaction is the actual catalyst, and because it is not improbable that in some cases the active substance is gradually changed during the course of vulcanization into an inactive product. Few or no investigations, however, have been made to determine the possibility of isolating quantitatively from a vulcanizate an accelerator originally introduced.

The number of compounds capable of accelerating vulcanization is so large, they vary so much in potency and in the character of their effects, and their potency is influenced so much by some components of rubber mixings other than rubber and sulfur, that the field which they present for both scientific and technical investigation is very large. Among the accelerators which are or have been most widely used in technical practice are the following: aniline, hexamethylenetetramine, anhydroacetaldehydeaniline, aldehyde ammonia, and thiocarbanilide. These may be considered as representative of the following three classes of substances in which many accelerators have been found: (1) bases; (2) condensation products of aldehydes with ammonia or amines; (3) thioureas. Most of the accelerators used technically are comparatively mild in their action. The order of their potency may be indicated roughly by saying that 1 per cent will reduce the time of vulcanization to one-half to one-sixth of that required in the absence of an artificial accelerator.

Ultra-Accelerators

Within the past three years or so the attention of investigators has been directed chiefly to classes of substances, the potency of which as vulcanization accelerators is of a much higher order than that just indicated. These more active agents have been distinguished from the milder ones by calling them "ultra-accelerators." Their activity is such that they can produce vulcanization with a proportion of sulfur which would be too small and at a temperature which would be too low for vulcanization in their absence. The term "ultra-accelerator" has been defined by the writer in the sense of this ability.[2] In the future the distinguishing prefix "ultra" may no longer be necessary, for the possibilities which such accelerators present are so valuable that probably they will in the course of time be the main class of accelerators used in practice. Their general employment will demand some modifications in present-day manufacturing operations and a great deal more study before completely satisfactory results can be obtained.

The degree of potency of ultra-accelerators may be illustrated by some data (obtained in conjunction with A. H. Smith) on the dithiocarbamate obtained by the addition of piperidine to carbon disulfide—piperidinium pentamethylenedithiocarbamate ($C_5H_{10}N.CS.SNH_2C_5H_{10}$).

Table I and Figs. 1 and 2 show the effect of one part of the accelerator on the vulcanization of a mixture (rubber, 90; sulfur, 10; zinc oxide, 10 parts) which is vulcanizable without an accelerator.

Table I—Vulcanization of Mixture A

Without Accelerator					With Accelerator				
Time Hours	T_B[a]	L_B[b]	$\frac{T_B \times L_B}{100}$[c]	L_{750}[d]	Time Minutes	T_B[a]	L_B[b]	$\frac{T_B \times L_B}{100}$[c]	L_{750}[d]
Cures at 141° C.									
1	1300	970	12,610	845	1	3440	810	27,864	585
2	1440	940	13,536	808	2	3125	685	21,406	466
3	2200	865	19,030	694	3	355	280	994	...
4	2000	815	16,300	643	5	300	205	615	...
Cures at 131° C.									
1	690	1060	7,314	(1084)	1	2740	850	23,290	659
2	1030	1030	10,609	968	2	3500	750	26,250	535
3	1093	971	10,613	891	3	3450	710	24,495	480
4	1410	930	13,113	813	5	365	290	1,058	...
5	1500	895	13,425	763	.	....	...	....	...

[a] Breaking stress in pounds per square inch.

[b] Percentage length at break.

[c] Tensile product.

[d] Percentage length at a load of 750 pounds per square inch.

At 141° C. (Fig. 1) vulcanization for 1 minute with the accelerator serves to bring the stress-strain curve to a lower position than vulcanization for 4 hours without it, and vulcan-

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[1] Bedford and Winkleman, in a paper presented before the Division of Rubber Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923; Seidl, *Gummi-Z.*, **25**, 710, 748 (1911); Scott and Bedford, This Journal, **13**, 125 (1921).

[2] *J. Soc. Chem. Ind.*, **42**, 369R (1923).

ization for 3 minutes with the accelerator results in a brittle product—that is, in a complete overcure. It would appear that without the accelerator a cure for about 300 minutes would be required to bring the curve to as low a position as that occupied by the curve obtained by vulcanization for 1 minute with the accelerator. Hence, the acceleration factor for 1 per cent of this accelerator in the mixture in question is about 300° at 141° C. At 131° C. (Fig. 2) vulcanization for 1 minute with the accelerator brings the curve into a lower position than vulcanization for 5 hours without it, and vulcanization for 5 minutes leads to a complete overcure. It would appear that without the accelerator a cure for nearly 7 hours would be necessary to bring the curve into as low a position as that occupied by the curve corresponding to the one obtained by curing for 1 minute with the accelerator.

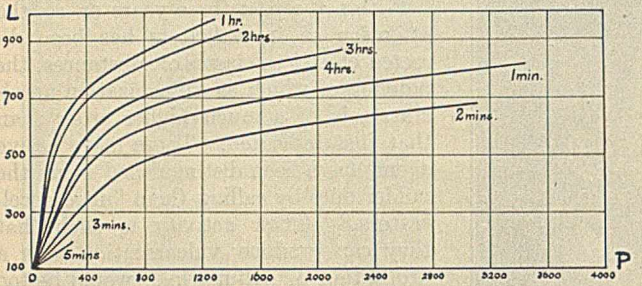

FIG. 1—VULCANIZATIONS AT 141° OF MIXTURE A (1 TO 4 HOURS WITHOUT ACCELERATOR; 1 TO 5 MINUTES WITH ACCELERATOR)

On the basis of the stress-strain curves, then, 1 per cent of the accelerator, in the presence of 10 parts of zinc oxide, increases the speed of vulcanization of a 90 : 10 rubber–sulfur mixture 300 to 400 times at temperatures from 131° to 141° C.

In Table II the potency of the accelerator is still more evident. This table shows the effect of one part of the accelerator on Mixture B (rubber, 90; sulfur, 2; zinc oxide, 10) which is for all practical purposes unvulcanizable in the absence of the accelerator.

TABLE II—VULCANIZATION OF MIXTURE B WITH ACCELERATOR

Time Minutes	T_B	L_B	$\frac{T_B \times L_B}{100}$	L_{750}
		Cures at 141° C.		
2	505	420	2,121	...
5	305	310	945	...
10	300	320	960	...
		Cures at 131° C.		
2	3630	850	30,855	583
5	3770	760	28,652	505
10	450	375	1,687	...
20	460	390	1,794	...
		Cures at 115° C.		
5	3500	855	29,925	617
10	4300	790	33,970	550
20	3930	740	29,082	485
30	4100	735	30,135	468
60	3180	670	21,306	468

Without the accelerator, heating for periods of 1, 2, 3, and 4 hours gave products which were practically unvulcanized, the highest value for T_B for any one sheet being less than 100 pounds per square inch.

In the absence of the accelerator the material remains practically unvulcanized after heating for 4 hours at 141° C. In its presence the stock is badly overcured by heating for 2 minutes at the same temperature and well cured by heating for 2 minutes at 131° F. or for 5 minutes at 115° F. The tensile strength obtainable in the vulcanized product is greatly increased by the use of the accelerator (Figs. 1 and 2).

Ultra-accelerators increase the speed of vulcanization so greatly that with their aid it becomes possible to vulcanize rubber mixtures at room temperatures. Their practical use for the cold vulcanization of rubber goods is as yet hardly beyond the experimental stage. A great deal of investigation must be conducted on the proportion of sulfur, choice of accelerator, proportion of accelerator, and composition of the mixture before the vulcanization of the various rubber mixtures in a tire, for example, can be satisfactorily and simultaneously conducted in the cold, to give a product possessing all possible improved physical properties and also aging well. But ultimately rubber manufacturers will probably find it possible to dispense with much of the expensive equipment now required for hot vulcanization.

Some evidence indicates that many accelerators improve the aging of vulcanized rubber, especially when the proportion of sulfur and accelerator is rightly balanced.[3] A more intensive study of the nature of aging is desirable. Marzetti[4] concludes that aging is essentially dependent upon the absorption of oxygen by rubber. It should be possible to choose accelerators of such a nature and to use them under such conditions that rubber goods with aging properties greatly superior to those of the products now usually made can be prepared.

One of the difficulties which may attend the practical employment of ultra-accelerators, because of the great activity of these substances, is "scorching," or premature vulcanization, during the mixing and other preliminary operations. This difficulty, however, is not likely to prove insuperable. Various preventative procedures have already been suggested.[5]

REACTIONS OF ULTRA-ACCELERATORS IN VULCANIZATION

The question of the reactions of accelerators during vulcanization raises some interesting points in organic chemistry. As Bedford and Sebrell[6] have remarked, while the reactions of organic compounds with sulfur have hitherto been of interest with respect to the sulfur colors, such reactions now become of interest with respect to the vulcanization of rubber. A study of the behavior of organic compounds, such as those employed as vulcanization accelerators, towards sulfur at temperatures lower than the temperatures used in the production of sulfur dyes is desirable.

Within the two or three years during which the reactions and mode of action of vulcanization accelerators have received attention, very satisfactory progress has been made. A scheme intended to cover a number of cases has been put forward by Bruni and Romani,[7] and a more comprehensive one by Bedford and his co-workers.[8] There are, however, many elements of speculation in both these schemes, which to a large extent must be regarded as merely suggestive of the types of reactions which accelerators probably undergo

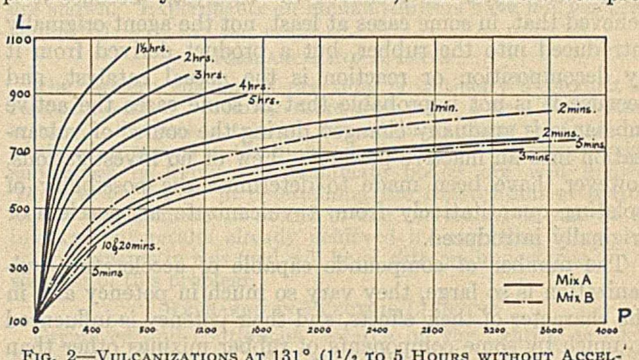

FIG. 2—VULCANIZATIONS AT 131° ($1^1/_2$ TO 5 HOURS WITHOUT ACCELERATOR; OTHER CURES WITH ACCELERATOR)

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[3] Schidrowitz and Burnand, *J. Soc. Chem. Ind.*, **40**, 268T (1921); Whitby and Walker, THIS JOURNAL, **13**, 816 (1921); Marzetti, *Giorn. chim. ind. applicata*, **5**, 122 (1923).

[4] *Loc. cit.*

[5] Pestalozza, *India-Rubber J.*, **65**, 623 (1923); Morton, U. S. Patent, 1,434,908 (1922); Romani, *Le Caoutchouc*, **19**, 11626 (1922).

[6] THIS JOURNAL, **13**, 1034 (1921).

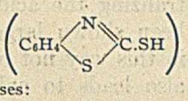
[7] Bruni and Romani, *India-Rubber J.*; Romani, *Le Caoutchouc*, **19**, 11626 (1922).

[8] THIS JOURNAL, **15**, 720 (1923).

in vulcanization and as offering working hypotheses on which to base a closer study of the various classes of compounds capable of accelerating vulcanization.

The most active accelerators known belong to the following classes of compounds:

1—Salts of dithiocarbamic acids from secondary amines ($R_2N.CS.SM$)
2—Dithio acids and their salts ($R.CS.SM$)
3—Xanthates ($RO.CS.SM$)
4—Mercaptobenzothiazoles and their mercaptides



$\left(C_6H_4\langle\overset{N}{\underset{S}{}}\rangle C.SH\right)$

5—Disulfides corresponding to the foregoing classes:
  (*a*) Thiuram disulfides ($R_2N.CS.S.S.CS.NR_2$)
  (*b*) Di-dithioacyl disulfides ($R.CS.S.S.CS.R$)
  (*c*) Dixanthogens ($RO.CS.S.S.CS.OR$)
  (*d*) Di-benzothiazole disulfides

Bruni and Romani[7] found that such disulfides are "auto-ultra-accelerators"—that is, they are capable of bringing about the rapid vulcanization of rubber in the absence of free sulfur.[9] These authors assume that this capacity is due to the splitting off of sulfur in an active form, accompanied by the conversion of the disulfide into a monosulfide.[10]

$$X.CS.S.S.CS.X \longrightarrow S + X.CS.S.CS.X$$

They also believe that the accelerating action of accelerators in the first four classes is dependent upon their conversion into the corresponding disulfides. This conversion they regard as being brought about by the action of sulfur on the zinc salt, the latter being the substance originally introduced or being formed from that substance by reaction with zinc oxide. The presence of this oxide is essential in order that all these accelerators may display their full activity.

$$(X.S)_2Zn + S \longrightarrow X.S.S.X + ZnS$$

Certain pieces of evidence tell against the correctness of this view. Bedford and Sebrell[11] find that zinc dimethyldithiocarbamate undergoes little or no reaction with sulfur when heated with it at vulcanization temperature (in boiling xylene). Although from the view stated above, it is reasonable to expect the disulfides to be somewhat more active than the zinc salts, it has been found[12] that the disulfides of Classes 5*a*, 5*b*, and 5*c* are appreciably less active than the corresponding zinc mercaptides of Classes 1, 2, and 3. Maximoff[13] has found that when they are melted with zinc oxide thiuram di- or monosulfides give zinc dithiocarbamates. Bedford and Sebrell[11] find that, whereas zinc dimethyl dithiocarbamate will vulcanize a rubber–sulfur–zinc oxide cement at room temperature, the corresponding thiuram disulfide fails to do so.

Bedford and Sebrell, however, state that in the presence of hydrogen sulfide the disulfide will vulcanize at ordinary temperature, which result they ascribe to the formation of the zinc dithiocarbamate, as follows:

$$X.S.S.X + H_2S \longrightarrow 2X.SH + S$$
$$2X.SH + ZnO \longrightarrow (X.S)_2Zn + H_2O$$

Maximoff[14] and Bedford[11] almost simultaneously expressed the view that in the case of all substances belonging to Classes 1 to 5, employed in the presence of zinc oxide, the active agent is the zinc salt.[15] In the case of Classes 1 to 4 the zinc salt is the substance originally introduced or is formed easily by reaction with zinc oxide. In the case of Class 5 the zinc salt is formed, according to Maximoff, by reaction with zinc oxide, and according to Bedford, by reaction with hydrogen sulfide and zinc oxide.

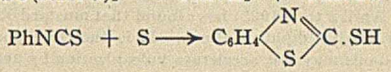
Other evidence supports the view that the zinc salts, and not the disulfides, are the active agents. Bedford supposes that the zinc salts function through the formation of polysulfides. While this is not improbable, there is as yet little direct experimental evidence in favor of this belief.

REACTIONS OF OTHER ACCELERATORS

Bruni and Romani have with some ingenuity sought to bring a large number of other types of accelerators within the same scheme as that which they propose for Classes 1 to 5, but all their suggestions call for closer investigation before they can be accepted. These authors give the following scheme for thiocarbanilide:

> Under the influence of heat the accelerator breaks down into phenyl mustard oil and aniline. The phenyl mustard oil then reacts with sulfur to give mercaptobenzothiazole, which, in the manner already suggested, is converted into the disulfide.

$$SC(NHPh)_2 \longrightarrow PhNH_2 + PhNCS$$



$$PhNCS + S \longrightarrow C_6H_4\langle\overset{N}{\underset{S}{}}\rangle C.SH$$

Since mercaptobenzothiazole can also be obtained by the action of sulfur on other disubstituted thioureas, on mono- and on trisubstituted thioureas, on dimethylaniline, and on methyleneaniline, Bruni and Romani consider that the accelerating action of all these substances can be brought into the same scheme. Romani[16] has suggested that the mode of action of accelerators, such as aldehyde ammonia, hydrobenzamide, and furfuramide, formed by the condensation of an aldehyde with ammonia, can be similarly envisaged. He suggests that such substances give rise to the aldehyde and ammonia, that the ammonia forms polysulfides with hydrogen sulfide generated during vulcanization,[17] and that the polysulfides form a dithio acid (accelerator of Class 3) with the aldehyde.

The case of thiocarbanilide has also been discussed by others. Kratz, Flower, and Coolidge[18] concluded that its

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[9] A point of some importance here is not clear—that is, whether such disulfides when used in the absence of free sulfur require zinc oxide to bring out their full curing power. Romani [*Giorn. chim. ind. applicata*, **3**, 197 (1921)] states that vulcanization by thiuram disulfides in the absence of free sulfur is rendered more energetic by the addition of zinc oxide, whereas Bedford and Sebrell [THIS JOURNAL, **14**, 25 (1922)] state that zinc oxide does not enhance the activity of these compounds.

[10] So far as the writer knows, it has not been experimentally demonstrated that the disulfides undergo conversion to monosulfides when heated. The method which has been used in the laboratory for this conversion has been treatment with potassium cyanide. Further, Bruni and Romani do not make it clear whether, when vulcanization is conducted in the presence of free sulfur, they regard the monosulfide, which they believe to be formed, as combining with sulfur to regenerate the disulfide and so activate the free sulfur. Vulcanization with a disulfide takes place much more quickly in the presence of zinc oxide and free sulfur than in the presence of zinc oxide alone. Furthermore, the monosulfides, although not quite so active as the disulfides, are, as Whitby and Simmons have recently found, powerful accelerators in the presence of zinc oxide.

In any case the question arises—what is the constitution of such organic disulfides? Are they Y.S.S.Y. or $Y.\overset{S}{\underset{S}{:}}Y$? If the former, the suggestion that they can split off sulfur and give monosulfides is less credible than if the latter. Their formation from thioles by oxidation would appear to indicate the former formula, whereas their conversion to monosulfides by treatment with potassium cyanide would appear to indicate the latter.

Bedford and Sebrell [THIS JOURNAL, **14**, 25 (1922)] agree with Bruni and Romani to the extent of concluding that one-quarter of the total sulfur of thiuram disulfides is available for vulcanization.

[11] THIS JOURNAL, **14**, 25 (1922).

[12] Whitby and Simmons, in a paper presented before the Division of Rubber Chemistry, at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[13] *Le Caoutchouc*, **18**, 10986 (1921).

[14] *Ibid.*, **18**, 10944, 10986 (1921).

[15] Earlier Bedford and Scott [THIS JOURNAL, **12**, 31(1920)] had expressed a different view as to the mode of action of dithiocarbamates. They supposed that at vulcanizing temperatures such compounds as the piperidinium salt of pentamethylenedithiocarbamic acid and the dimethylammonium salt of dimethyldithiocarbamic acid lose hydrogen sulfide to give thioureas. Apparently, at this time the important relation of zinc oxide to such accelerators was not recognized.

[16] *Le Caoutchouc*, **19**, 11626 (1922).

[17] This reaction has been described as a method of preparing dithio acids by Bruni and Levi [*Atti accad. Lincei*, [5] **32**, 5 (1923)].

[18] THIS JOURNAL, **12**, 317 (1920).

action is dependent essentially upon the aniline formed by its decomposition into aniline and phenyl mustard oil. They considered the latter substance to be inactive.[19] Bedford and Sebrell[6] believe that thiocarbanilide accelerates vulcanization by reacting, in its tautomeric form, PhN: C-(SH).NHPh, to form a zinc mercaptide, which, as in the case of Classes 1 to 5, they believe to be the active substance. These authors state that the formation of mercaptobenzothiazole from thiocarbanilide under the influence of heat and sulfur does not occur, as the views of Bruni and Romani would demand, at the temperature of vulcanization. They quote some suggestive experiments in support of their view.

The ideas of Bedford have undergone much modification during their development, but his final belief apparently is that most cases of acceleration are due to polysulfide formation on the part of the thiole[20] or disulfide[21] groups.

Some investigators[14,11] hold that an important factor in the ability of certain compounds containing an —SH group to act as accelerators and of certain metallic oxides to "activate" such compounds is the stability of the mercaptides in question. Yet recent experiments[22] show that, although the heavy metal salts of accelerators in Classes 1 to 4 are distinguished in general by remarkable stability, the mere ability to form mercaptides, even of zinc, which are stable at vulcanizing temperatures is not enough to confer accelerating power, as some stable mercaptides, such as zinc phenylthiobiazolthione mercaptide, have little or no accelerating power.

DISPERSING AGENTS AS ACCELERATORS

Recent experiments[23] have introduced a new factor for consideration with respect to the mechanism of accelerator action. They make it appear that in some cases accelerators may owe part or all of their effect on the rate of vulcanization, not to action on the sulfur, but to action on the caoutchouc.[24] It has been shown that soaps hasten vulcanization in the presence of recognized vulcanization accelerators.[25] Their effect is presumably to increase the degree of dispersion of the caoutchouc, or of its sulfur reaction product.

Many accelerators are bases,[26] others, like aldehyde ammonia, may give rise to bases by decomposition; and others, like piperidinium pentamethylenedithiocarbamate, may give rise to bases as a result of reaction with zinc oxide. Such bases, if sufficiently strong, will give rise to soaps by neutralizing the acids of which the rubber resin has recently been shown largely to consist.[27] The formation of soaps in this way not only increases the rate of vulcanization, but also leads to enhanced tensile strength in the vulcanized product.[28]

The action of an accelerator such as piperidinium pentamethylenedithiocarbamate is believed to depend upon the formation of two substances—(1) the zinc dithiocarbamate, and (2) piperidinium salts (soaps) of the resin acids. Representing the acids of the rubber resin as HA, the reactions which probably occur in a rubber stock containing zinc oxide and an accelerator of the type just mentioned may be shown as follows:

$$2C_5H_{10}N.CS.SNH_2C_5H_{10} + ZnO + 2HA \longrightarrow (C_5H_{10}N.CS.S)_2Zn + 2A.NH_2C_5H_{10} + H_2O$$

It is probable that some of the phenomena in rubber which have been described as "depolymerization" and "polymerization" are in reality merely changes, such as those caused by the introduction of soaps, in the degree of dispersion of the caoutchouc.

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[19] Whitby and Dolid (paper presented before the Division of Rubber Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923) have found that mustard oils dissolve rubber to give strikingly limpid solutions. It is therefore possible that, although mustard oils may not accelerate vulcanization by activating sulfur, they may do so by increasing the degree of dispersion of caoutchouc.

[20] The —SH group may be originally present in the molecule, as in the case of Classes 1 to 4, or it may be formed by tautomerization, as in the case of thiocarbanilide. Whitby and Simmons report that in general where the occurrence of an —SH group depends upon tautomerization, accelerating power is absent or comparatively low. In an earlier paper [Scott and Bedford, THIS JOURNAL, **13**, 125 (1921)] it was suggested that in the case of a large number of accelerators —SH groups arise by the addition of hydrogen sulfide to ammonia or an amine, and such accelerators were described as "hydrogen sulfide polysulfide" accelerators. But apparently this suggestion has been modified or abandoned.[6]

[21] In some cases disulfides are supposed to be formed by sulfur reaction. Yet, while in the case of accelerators of Class 5, acting in the presence of zinc oxide, this author regards disulfides as being reduced to thioles prior to polysulfide formation, in the case of the disulfides which he regards as being formed by sulfur reaction from such accelerators as aromatic diamines,[6] and in the case of accelerators of Class 5; acting in the absence of zinc oxide,[11] he regards the disulfides themselves as undergoing polysulfide formation.

[22] Whitby and Simmons, *loc. cit.*; Whitby, *Roy. Soc. Canada*, May, 1923.

[23] Whitby and Cambron, *J. Soc. Chem. Ind.*, **42**, 333T (1923); Whitby and Simmons, *loc. cit.*

[24] Some indirect evidence for the view that accelerators may affect the rubber rather than the sulfur was advanced by Le Blanc and Kröger [*Z. Elektrochem.*, **27**, 335 (1921)]. These authors found, in experiments on the rate of gel formation in rubber-sulfur cements, that solvents of high dielectric constant, giving rubber solutions of low viscosity (solutions in which the rubber is "depolymerized"), led to a more rapid gelling than solvents of lower dielectric constant, giving solutions of higher viscosity, and that accelerators both reduced the viscosity and hastened gel formation.

[25] Ultra-accelerators were used, but it is probable that soaps have a similar effect on vulcanization in the presence of milder accelerators and of the accelerators naturally present in raw rubber.

[26] Caustic alkalies act as vulcanization accelerators. Twiss [*J. Soc. Chem. Ind.*, **36**, 782 (1917)], who is responsible for the most complete study of caustic alkalies as accelerators, mentioned the possibility of such accelerators functioning by acting on the rubber rather than on the sulfur. Twiss and Thomas [*Ibid.*, **40**, 48T (1921)] disproved the suggestion that the accelerating action of caustic alkalies and other bases is due to their catalytic effect on the transformation of S_μ into $S\lambda$. Scott and Bedford [THIS JOURNAL, **13**, 125 (1921)] regarded caustic alkalies as functioning through the formation of polysulfides on the part of the hydrosulfides supposed to arise from them by the action of hydrogen sulfide. Bedford and Sebrell[6] considered the action of sodium phenolates as accelerators to be due to reaction of sulfur with the aromatic nucleus leading to a disulfide—for example, $NaO.C_6H_4.S.S.C_6H_4.ONa$, from which polysulfides are formed.

[27] Whitby and Winn, *J. Soc. Chem. Ind.*, **42**, 336T (1923).

[28] This observation may prove to be of significance with regard to the question of the structure of elastic gels.

Huge Sale of Pulp Timber by Forest Service

The largest sale of pulp timber ever made by the United States Forest Service was announced recently. The transaction involves 334,000,000 cubic feet of timber in the Tongass National Forest, Alaska. The buyer, the firm of Hutton, McNear & Dougherty, of San Francisco, has agreed as part of the consideration for the timber to build a pulp manufacturing plant of not less than 100 tons daily capacity, and ultimately with a daily capacity of 200 tons, at the Cascade Creek water-power site on Thomas Bay, 20 miles from Petersburg, Alaska, within the Tongass National Forest. It is understood that the firm plans to instal a complete newsprint plant with a daily capacity of 200 tons.

According to the plans of the Forest Service for this sale unit, as well as for all pulp timber developments in Alaska, the timber will be cut on a perpetual supply basis, enough seed trees being left to insure complete natural reproduction. The volume of pulp timber and the area of timber-growing land within the unit, reserved from other disposition, are sufficient to afford a permanent source of raw material for this enterprise.

Under the perpetual timber supply plan at least 1,500,000 tons of paper can ultimately be produced in Alaska every year. This amount is more than one-half of the newsprint now consumed annually in the United States and nearly 20 per cent of the total consumption of all kinds of paper and wood fiber products. As each new unit of timber and water power is developed in Alaska, the manufacturing capacity will be gaged to the timber supply and growing power of the land so that there will be no depletion of raw material.

The Cascade Creek sale is in line with the policy for the development of the national forest in Alaska, which was a subject of special study by President Harding during his trip to the Territory and which received his indorsement.

1—Mercaptobenzothiazole and Its Derivatives as Accelerators of Rubber Vulcanization[1,2,3]

By L. B. Sebrell and C. E. Boord

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In a separate paper[2] the preparation and properties of 1-mercaptobenzothiazole and six of its substituted derivatives have been fully described. Three of these methods are new. The mechanism of the reactions involved in these preparations has been fully discussed. For six of these mercaptothiazoles the disulfides have also been described, and in two cases the zinc and lead salts.

Mercaptobenzothiazole and its substituted derivatives show the following relative activity as accelerators of vulcanization: (1) 3-methyl, (2) 3,5-dimethyl, (3) unsubstituted, (4) 4-methyl, (5) 5-methyl, (6) 5-ethoxy, (7) 5-methoxy. Several compounds with a structure analogous to 1-mercaptobenzothiazole were prepared and their accelerating values determined. The mercaptobenzothiazoles have no value as accelerators except in the presence of zinc oxide. The zinc and normal lead salts of these thiazoles are faster curing than the corresponding free thiazoles. The zinc salt of the 1-mercapto-5-methylbenzothiazole and the normal lead salt of 1-mercapto-3-methylbenzothiazole gave the highest accelerating values of any of the compounds tested. The disulfides have a lower curing power than the corresponding free thiazoles. The accelerating power of the mercaptobenzothiazoles is directly connected with the atomic grouping $—S—\overset{\|}{C}—SH$. *Any alteration in this grouping removes almost entirely the power to accelerate rubber vulcanization. The mercapto group is more essential to the accelerating action than the sulfur atom of the thiazole ring. Both are necessary to develop the highest accelerating power. Aliphatic mercaptothiazoles show marked accelerating power but are inferior to the mercaptobenzothiazoles. The metallic salts of the mercaptobenzothiazoles are assumed to be the active agents in producing acceleration.*

The existing theories for the mechanism of acceleration by mercapto compounds have been given. The results obtained in this work are correlated with the Bedford and Sebrell polysulfide theory.

THE use of 1-mercaptobenzothiazole as an accelerator of vulcanization was first suggested by Bedford and Sebrell.[4] This announcement was closely followed by that of Bruni and Romani,[5] who set forth in detail a method for the preparation of 1-mercaptobenzothiazole by heating thiocarbanilide with sulfur under pressure. They also proposed a theory for the mechanism of the accelerating action as applied to thiocarbanilide and the thiazole derivatives.

The second paper of Bedford and Sebrell[6] revealed that the method of preparation described by Bruni and Romani had previously been known to them, and pointed out that the mechanism used by the latter workers to explain the action of thiocarbanilide as an accelerator was untenable.

The present investigation is a continuation of the work of Bedford and Sebrell. It has been carried out with the following purposes in mind:

1—To make a comparative study of the relative value of several derivatives of 1-mercaptobenzothiazole as accelerators of vulcanization.

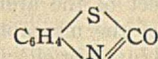
2—By a process of substitution and elimination to determine what part of the mercaptobenzothiazole structure is responsible for the accelerating action of these compounds.

Preparation of Materials

1-Mercaptobenzothiazole and Its Derivatives—The preparation and properties of 1-mercaptobenzothiazole and its 3-methyl, 4-methyl, 5-methyl, 3,5-dimethyl, 5-methoxy, and 5-ethoxy derivatives have been fully described in a separate paper by the present authors.[2] Each of these compounds, with two exceptions where the quantity of material was limited, was prepared by four methods. The methods were all alike in that the reaction mixtures were heated together in an autoclave under pressure. The mixtures were (1) the corresponding disubstituted thiourea and sulfur, (2) the zinc salt of the corresponding aryldithiocarbamic acid and sulfur, (3) the ammonium salt of the same acid and sulfur, and (4) a mixture of the corresponding aryl amine, carbon disulfide and sulfur.[7]

The first of these methods is the same as used by Bedford and Sebrell[4] and by Bruni and Romani[5] to prepare 1-mercaptobenzothiazole. It was extended by the present authors[8] and also by Romani[9] to the monomethyl derivatives of this same thiazole. The disulfides of the unsubstituted thiazole and each of its methylated derivatives were described, as well as the normal zinc, normal lead, and basic lead salts of the same thiazole and its 3-methyl derivative and the normal zinc salt of the 5-methyl derivative. For the details of these preparations it will be necessary to consult the original article.

Other Benzothiazole Derivatives—In order to determine the particular grouping in the 1-mercaptobenzothiazole structure responsible for the accelerating action, it became necessary to prepare a series of related benzothiazole derivatives. In each case these compounds differed from the true 1-mercaptobenzothiazole by a single atom or grouping, the remaining part of the molecular structure being identical. All these substances have been previously described, but the details of their preparation are incomplete.

1-Hydroxybenzothiazole,[10]  $C_6H_4{<}\genfrac{}{}{0pt}{}{S}{N}{>}COH$, was prepared

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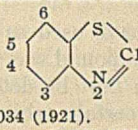
[1] Presented before the Division of Rubber Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

[2] This paper and one entitled: "The Preparation and Properties of 1-Mercaptobenzothiazole; Its Homologs and Derivatives," being published simultaneously in *J. Am. Chem. Soc.*, **45**, 2390 (1923), have been abstracted from the dissertation presented by L. B. Sebrell to the Graduate School of Ohio State University in partial fulfilment of the requirements for the degree of doctor of philosophy, September, 1922.

[3] The remarks of Bogert and Meyer, *J. Am. Chem. Soc.*, **44**, 826 (1922), concerning the numbering and nomenclature of the benzothiazole derivatives, have been noted with some interest. Their contention that all the atoms of the thiazole ring should be numbered is correct, but for the sake of uniformity the present authors prefer to adhere to the system in use by *Chemical Abstracts*. For this reason, the system as outlined by Decennial Index of *C. A.*, **1**, 2345 (1907–1916)—namely, omitting the sulfur and beginning the numbering with the carbon atom of the thiazole ring—has been followed.



[4] This Journal, **13**, 1034 (1921).

[5] *Giorn. chim. ind. applicata*, **3**, 196 (1921).

[6] This Journal, **14**, 25 (1922).

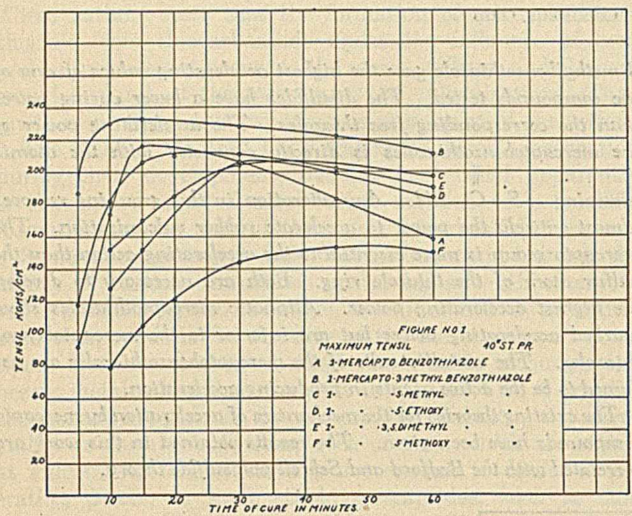
[7] This method was suggested by W. J. Kelly of the Goodyear Tire & Rubber Company.

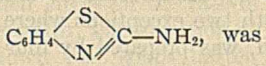
[8] *Science*, **56**, 55 (1922).

[9] *Gazz. chim. ital.*, **52**, 29 (1922).

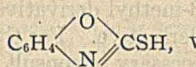
[10] *Ber.*, **12**, 1126 (1879); **13**, 9 (1880).

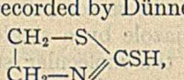
by the hydrolysis of 1-chlorobenzothiazole, according to the method described by Hofmann.[10] Long heating of the free 1-chlorobenzothiazole does not accomplish the hydrolysis. However, if the hydrogen chloride addition product of 1-chlorobenzothiazole is heated with alcohol for 40 hours, the hydrolysis is almost complete. The solution was rendered strongly acid and precipitated by dilution with water. After two recrystallizations from 75 per cent alcohol 1-hydroxybenzothiazole was obtained as white needles melting at 136° C. This is the same melting point as given by Hofmann. The hydrolysis of the hydrochloride may be accomplished in a much shorter time by heating with alcohol under pressure.



1-Amidobenzothiazole,  $C_6H_4\langle{}^{S}_{N}\rangle C{-}NH_2$, was first prepared by Hofmann[11] by the action of alcoholic ammonia on 1-chlorobenzothiazole at 160° C. In this laboratory the method, as described, always yields the product in the form of a noncrystallizable sirup. Excellent results were obtained by the following method:

Fifteen grams of the 1-chlorobenzothiazole together with 45 cc. of saturated alcoholic ammonia and 15 cc. of aqueous ammonia were sealed in a tube and heated at 200° C. for 4 hours. On opening the tube the contents were mixed with 50 per cent alcohol, strongly cooled in an ice bath and diluted very slowly with water to 1 liter. After standing in an ice box for 12 hours 1-amidobenzothiazole was deposited as fine white needles, with only a trace of the sirupy impurity. The yield was 10 grams. This product after recrystallization from benzene melted at 127° C., compared with 129° C. recorded by Hofmann.

1-Mercaptobenzoxazole,  $C_6H_4\langle{}^{O}_{N}\rangle CSH$, was prepared by refluxing an alcoholic solution of *o*-aminophenol with carbon disulfide according to the method of Dünner.[12] After the preliminary purification by precipitating from sodium carbonate solution, and recrystallization from water, the product melted at 193° C., the same as recorded by Dünner.

μ-Mercaptothiazolen,  $\begin{array}{l} CH_2{-}S \\ \vert \\ CH_2{-}N \end{array}\rangle CSH$, was prepared for the purpose of comparison with 1-mercaptobenzothiazole to determine the effect of the aromatic nucleus upon the accelerating power of the mercaptothiazoles. The compound was first described by Gabriel[13] who prepared it by the action of β-bromoethylamine hydrochloride and carbon disulfide in alkaline solution. Some difficulty was experienced in the isolation of both the hydrobromide and its reaction product with carbon disulfide, but a sufficient quantity was finally obtained to determine its relative value as an accelerator.

Results of Compounding Tests

All the compounds listed above were tested to ascertain their relative value as accelerators of vulcanization. The following experimental formula was used:

100.00 parts of rubber (smoked sheet)
5.00 parts of zinc oxide
3.50 parts of sulfur
1.00 part of 1-mercaptobenzothiazole or a molecular equivalent of its derivative or analog

With a few exceptions, each of these compounds produced very rapid curing in the formula given.

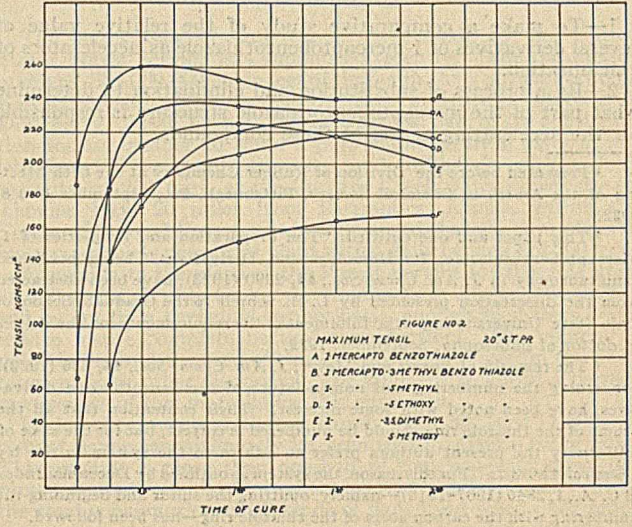
Since many of these substances are rapid and powerful accelerators, slight variations in the milling and curing may produce differences of some magnitude in the tensile-time diagrams. For this reason the conditions of milling and curing were standardized as follows:

The stocks were all mixed in 1-kg. batches on a small experimental mill. After milling for 20 minutes to break down the rubber, the zinc oxide and accelerator were added and mixed thoroughly into the stock for 10 minutes. The stock was then cooled to the lowest workable temperature and the sulfur added. After 5 minutes further mixing it was removed from the mill. All samples were milled as nearly as possible as described above.

The curing was conducted in a steam platen press in which the temperature was controlled as closely as possible. All cures were made in the same set of molds, which had been preheated before use by allowing them to remain for at least 30 minutes in the press at the required temperature. All the cures were made using the same decks of the same press. The vulcanized sheets after being removed from the molds were plunged into a tank of cold water to stop vulcanization.

The physical data given in the following tables were obtained by two observers on a Scott testing machine using dumb-bell test pieces. The average of two or more closely agreeing strips is given for each cure.

The results of the physical tests on the cures made with 1-mercaptobenzothiazole, its alkyl and alkyloxy derivatives, are recorded in Table I, and are represented graphically in Figs. 1 and 2. In comparing the relative activity of these compounds, the writers have used as a basis of comparison the time in which each compound was judged to give the best technical cure. This can best be determined by subjecting the stocks themselves to certain arbitrary tests, such as the effect of repeated flexing and resistance to tear. The nature of the grain as indicated by the appearance of the tear is also



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[11] *Ber.*, **13**, 11 (1880).

[12] *Ibid.*, **2**, 465 (1876); **16**, 1825 (1883).

[13] *Ibid.*, **21**, 566 (1888); **22**, 1137, 1152 (1889).

TABLE I—PHYSICAL TESTS—STOCKS CURED WITH MERCAPTOBENZOTHIAZOLES

ACCELERATORS	Time of Cure Min.	100%	200%	300%	400%	500%	600%	700%	800%	Bk.	Elong.	Tensile Product	Energy of Resilience	STATE OF CURE
40 pounds steam pressure (141° C.)														
1-Mercaptobenzothiazole	5	2.5	3	4	6	7	12	21	48	92	900	82.8	149.5	Under
	10	4	7	10.4	16	24	46	105	160	174	810	141.0	309	Best
	15	5	12	15	23	33	70	140	...	216	780	168.5	370	Slightly over
	30	4.5	8	13	20	36	75	150	...	206	780	161.0	374	Over
	45	5	9	12.5	21	34	66	125	...	183	770	141.0	318	Over
	60	5	9	12	19	34	55	114	...	158	770	121.7	286	Over
1-Mercapto-3-methylbenzothiazole	5	5	7	12	18	26	58	124	187	187	800	149.5	343	Slightly over
	10	7	10	17	25	43	85	167	...	230	780	179.5	330	Slightly over
	15	7	11	17	24	46	84	165	...	233	750	175.0	371	Over
	20	7	11	17	24	40	83	152	...	224	780	175	408	Over
	30	6	10	14	24	39	73	154	...	228	750	170	338.5	Over
	45	6	10	16	24	45	83	161	...	222	780	173	418	Over
	60	5	7	12	19	30	54	112	...	211	800	169	344	Over
1-Mercapto-5-methylbenzothiazole	10	4	5	7	12	15	27	65	122	152	860	131	278	Under
	15	4	6	8	12	19	36	82	151	170	830	141	290.6	Slightly under
	20	5	6	11	14	24	46	100	177	185	810	150	312.6	Very slightly over
	30	4	7	12	17	25	46	188	...	204	780	159	317	Very good over
	45	5	8	12	18	30	60	127	...	193	780	150.5	320.5	Over
	60	5	7	12	18	30	66	114	183	197	820	161	381.5	Over
1-Mercapto-5-ethoxybenzothiazole	10	4	6	8	12	17	28	58	99	128	850	109	239	Under
	15	4	6	11	15	24	44	95	149	157	815	128	296	Veryslightlyunder
	30	4	7	14	18	31	62	124	206	206	800	165	363	Over
	45	5	8	12	19	31	60	123	199	199	800	159	358	Over
	60	5	7	12	18	25	47	94	166	184	825	152	335	Over
1-Mercapto-5-methoxybenzothiazole	10	1	3	4	5	7	12	19	36 $\frac{900}{72}$	79	975	105	179.6	Under
	15	3	4	6	7	12	18	36	66	106	900	94.5	204	Under
	20	4	5	7	10	15	24	47	90	121	860	104	220	Under
	30	4	6	10	12	23	42	83	...	144	780	112	230	Under
	45	3	6	9	14	20	34	69	132	153	860	132	306.5	Fair
	60	4	6	10	12	22	40	78	144	150	820	123	273	Good
1-Mercapto-3-5-dimethylbenzothiazole	5	3	4	6	7	11	18	32	74	118	890	105	204	Under
	10	5	6	11	16	23	46	108	172	182	810	143	319	Very slightly over
	15	4	6	11	17	25	50	120	206	206	800	165	336	Over
	20	5	9	14	23	39	77	142	...	210	780	164	379	Over
	30	5	10	13	21	38	77	149	211	211	800	169	419	Over
	45	5	7	12	18	30	54	113	178	202	825	167	375.5	Over
	60	6	7	12	19	30	59	108	...	190	790	150	321	Over
20 pounds steam pressure (125° C.)														
1-Mercaptobenzothiazole	10	1	2	3	4	5	6	8	12	13	820	10.7	60	Under
	20	4	6	10	15	21	41	78	152	184	845	155	326.6	Slightly under
	30	5	8	14	20	31	68	135	230	230	800	184	401	Best
	60	5	10	16	24	44	90	174	...	236	760	179	399	Over
	90	5	10	16	25	44	92	174	...	232	770	178	421	Much over
	120	5	10	17	25	46	87	173	...	232	770	178	417	Much over
1-Mercapto-3-methylbenzothiazole	10	4	8	10	16	22	41	89	168	187	830	155	318	Slightly under
	20	5	10	16	24	40	75	146	...	248	790	196	320	Slightly over
	30	6	12	19	29	50	103	205	...	260	750	195	437	Over
	60	6	11	19	31	54	110	214	...	252	740	187	431	Over
	90	6	14	20	30	50	110	216	...	240	730	175	406	Much over
	120	6	14	20	30	54	110	187	...	240	730	175	391	Much over
1-Mercapto-5-methylbenzothiazole	20	3	5	8	10	15	26	47	93	140	900	126	277	Under
	30	5	8	10	15	25	48	99	174	174	800	139	337	Under
	60	5	10	16	21	33	76	144	...	220	790	166	397	Good, slightly over
	90	5	10	15	24	38	74	150	...	227	790	172	410	Over
	120	5	10	15	25	42	76	166	...	213	760	162	369	Over
1-Mercapto-5-ethoxybenzothiazole	20	3	5	8	10	15	26	50	101	140	890	125	276	Under
	30	5	6	10	14.5	21	35	75	146	182	860	157	338	Slightly under
	60	5	10	12	20	31	62	135	...	195	770	150	323	Best
	90	5	10	15	22	35	71	134	...	218	770	168	348	Over
	120	5	10	15	24	41	85	152	...	210	780	164	401	Over
1-Mercapto-5-methoxybenzothiazole	20	2	3	4	5	6	10	16	25	64	980	62.7	139	Very much under
	30	3	4	5	8	12	21	40	72	116	900	105	223	Much under
	60	5	7	10	15	21	36	78	136	142	830	118	282	Fair
	90	4	6	10	16	25	46	93	...	165	800	132	283	Fair
	120	5	9	15	20	30	54	108	...	168	780	131	297	Best
1-Mercapto-3-5-dimethylbenzothiazole	10	2	3	4	5	7	11	18	34	68	940	64	136	Under
	20	4	8	12	17	25	56	112	...	185	790	146	312	Good, slightly under
	30	6	10	15	21	36	74	153	...	211	765	162	475	Good, slightly over
	60	5	10	16	26	46	102	200	...	225	740	167	390	Over
	90	5	10	18	27	48	98	185	...	194	720	140	336	Much over
	120	5	10	16	26	46	92	183	...	199	740	147	363	Much over

taken into consideration. The results of such tests are given for each cure in the tables in the column "State of Cure." In some cases the cures were not sufficiently close so that, for example, a 5-minute cure might be judged by means of these tests to be undercured, while a 10-minute cure would be considerably overcured. In such cases the writers have interpolated for the time of best technical cure.

The relative order of activity of these compounds as accelerators cannot well be determined from a comparison of the maximum tensiles obtained, since the test sheet which would give the highest tensile is in almost all cases overcured from a practical standpoint. Any attempt to classify the compounds on the basis of the so-called optimum cure, as given by either the maximum tensile product or the energy of resilience, or a combination of these factors, would be subject to the same objection as given above for the classification in order of maximum tensile.

If it is desired to utilize the stress-strain data in determining the relative activity of these compounds, they can, for example, be ranked in the order of the highest tensile stress at 700 per cent elongation given by a 10-minute cure on each compound at 40 pounds steam pressure. In this way the errors inherent in a determination of the maximum tensile are avoided. If such a classification is made it will be found that the compounds arrange themselves in exactly the same order as determined by the best technical cure.

The writers are therefore inclined to classify the various mercaptobenzothiazoles according to the time necessary to produce the best cure from a practical standpoint as shown by the above arbitrary tests, and to use the stress-strain data as a measure of the quality of the stocks.

It is realized that the present method of determining the relative activity might not seem satisfactory to all, and for this reason the complete data for the physical tests, together with the tensile product and the energy of resilience, have been included in the tables.

Since only one formula was used in testing all these accelerators and because in some cases an insufficient number of cures have been obtained, it is obvious that the results herein presented cannot be considered as representing a complete or detailed compounding investigation. They are, however, considered satisfactory from the standpoint of determining the relative activity of the various mercaptobenzothiazoles and their derivatives as accelerators.

Fig. 1 shows the tests made on cures at 40 pounds steam pressure, while Fig. 2 gives the same data for cures at 20 pounds steam pressure. The relative activity of the 1-mercaptobenzothiazoles and the time required to produce the best technical cure are given in Table II.

TABLE II—ORDER OF REACTIVITY OF THE 1-MERCAPTOBENZOTHIAZOLES AS ACCELERATORS

SUBSTANCE	40 Pounds Pressure		20 Pounds Pressure	
	Time of Best Technical Cure	Order of Activity	Time of Best Technical Cure	Order of Activity
1 - Mercapto - 3 - methylbenzothiazole	5 min.	1	18 min.	1
1 - Mercapto - 3,5 - dimethylbenzothiazole	8 min.	2	25 min.	2
1-Mercaptobenzothiazole	10 min.	3	30 min.	3
1 - Mercapto - 5 - methylbenzothiazole	18 min.	4	55 min.	4
1 - Mercapto - 5 - ethoxybenzothiazole	20 min.	5	60 min.	5
1 - Mercapto - 5-methoxybenzothiazole	1 hr.	6	2 hrs.	6

The data showing the relative curing power of 1-mercapto-4-methylbenzothiazole are not given in Table II. A limited supply of this material prevented it from being included when the foregoing tests were made. It had previously been tested in a different formula. Under these conditions its activity as an accelerator was found to lie between the 5-methyl and 3-methyl derivatives, being very close to that of 1-mercaptobenzothiazole.

In the absence of zinc oxide the 1-mercaptobenzothiazoles are without appreciable accelerating action. Compounded in the foregoing formula, except that the zinc oxide was omitted, 1-mercaptobenzothiazole cured at 40 pounds steam pressure for 2 hours gave a maximum tensile strength of 96 kg. per sq. cm. Curing the same mixture at 20 pounds steam pressure for the same time gave a maximum tensile strength of 50 kg. per sq. cm. These substances, therefore, have no practical value as accelerators except in the presence of zinc or lead oxides. From these results it seems probable that in the process of vulcanization the mercaptobenzothiazoles are converted into the corresponding zinc salts, these salts acting as the true accelerating agents. To test this assumption the zinc and lead salts of 1-mercapto-, 1-mercapto-3-methyl, and 1-mercapto-5-methylbenzothiazoles were tested in the foregoing formula. The results are shown in Tables III*a* and III*b* and the tensile–time curves in Figs. 3 and 4.

The zinc salt of the 5-methyl derivative is slightly faster in its curing action than the zinc salt of the free 1-mercaptobenzothiazole or its 3-methyl derivative. The last two are about equal in curing power. On the other hand, the lead salt of the 3-methyl derivative is the most active of the three lead salts, giving good cures in 15 minutes at 20 pounds steam pressure. The two remaining lead salts are about equal in activity but vary in the tensile strengths produced.

In all cases the zinc and lead salts of these mercaptobenzothiazoles are much more powerful accelerators than the corresponding free compounds. The zinc salt is, generally, more powerful than the corresponding lead salt. These metallic salts must also be used with additional metallic oxide to obtain their maximum accelerating power.

The disulfides of the several mercaptobenzothiazoles were also tested in the foregoing formula, and were found to be considerably less active than the free thiazoles.

Two conclusions may be drawn from these facts:

1—The 1-mercaptobenzothiazoles when used as accelerators first form the metallic salts by action with the metallic oxide present. These salts are the active accelerators.

2—The salts so formed tend to decompose during the process of vulcanization and an excess of the metallic oxide must be present to reform the salts and thus maintain the accelerating action.

TABLE III*a*—PHYSICAL TESTS: STOCKS CURED WITH THE ZINC SALTS OF MERCAPTOBENZOTHIAZOLE

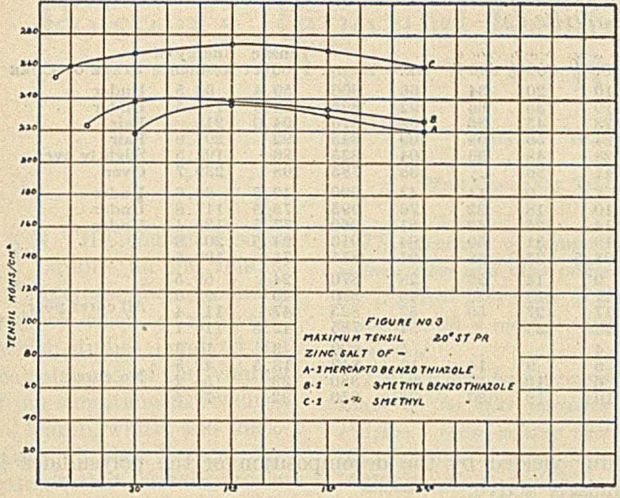
20 pounds steam pressure (125° C.)

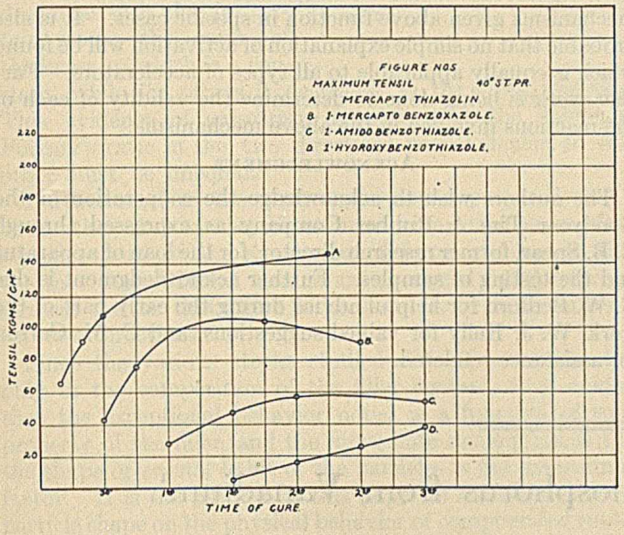
ACCELERATOR	Time of Cure Min.	100%	200%	300%	400%	500%	600%	700%	800%	Bk.	Elong.	Tensile Product	Energy of Resilience	STATE OF CURE
1-Mercaptobenzothiazole	30	8	13	20	29	52	109	202	...	218	720	155	374	Over
	60	8	14	22	36	64	127	221	...	236	715	169	415.8	Over
	90	9	14	23	39	67	130	219	...	229	715	163	425	Over
	120	9	14	23	37	64	125	206	...	220	720	158	417.6	Over
	180	8	14	21	33	55	106	188	...	210	720	151	370.8	Over
1-Mercapto-3-methylbenzothiazole	15	6	10	15	39	53	104	198	...	223	750	167	431	Good
	30	6	11	21	38	73	141	219	...	238	740	167	490.9	Over
	60	6	12	21	36	62	120	218	...	238	730	174	434.4	Over
	120	6	12	18	32	57	108	200	...	226	740	167.5	418	Over
	180	6	12	19	33	57	107	190	...	220	740	163	493	Over
1-Mercapto-5-methylbenzothiazole	5	5	9	13	21	37	67	133	220	253	825	204	454	Slightly under
	10	5	9	13	22	40	80	142	...	260	855	222	350.5	Under
	30	6	10	18	26	52	102	183	...	268	850	228	418	Over
	60	6	12	20	30	60	114	208	...	274	745	204	454	Over
	120	6	13	20	34	62	114	211	...	260	730	190	425	Over
	180	5	10	20	32	60	104	185	...	238	760	181	450.4	Over

TABLE III*b*—PHYSICAL TESTS: STOCKS CURED WITH NORMAL LEAD SALTS OF MERCAPTOBENZOTHIAZOLES

20 pounds steam pressure (125° C.)

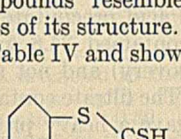
ACCELERATOR	Time of Cure Min.	100%	200%	300%	400%	500%	600%	700%	800%	Bk.	Elong.	Tensile Product	Energy of Resilience	STATE OF CURE
1-Mercaptobenzothiazole	15	7	8	12	18	30	58	108	...	142	760	108	232	Good
	30	6	11	16	25	42	78	145	...	181	740	134	315.7	Over
	60	7	12	18	39	46	97	165	...	202	710	144	319.8	Over
	90	6	11	18	39	46	86	160	...	206	750	155	377.5	Over
	120	6	11	17	27	24	81	141	...	202	760	154	339.4	Over
	180	7	10	15	25	40	70	129	...	183	780	143	356	Over
1-Mercapto-3-methylbenzothiazole	15	5	9	16	26	45	92	162	250	260	835	217	551	Good
	30	5	9	17	27	46	97	175	...	255	752	192	400	Over
	60	7	11	17	28	48	102	186	...	248	785	193	490.5	Over
	120	6	12	19	29	50	105	190	...	241	745	179	413	Over
	180	6	10	20	30	54	106	186	...	238	767	182	461	Over
1-Mercapto-5-methylbenzothiazole	10	3	5	7	9	10	18	36	60 $\frac{900}{100}$	113	960	108.5	261.9	Under
	25	5	9	14	20	25	60	120	...	180	790	142	328	Good
	60	5	10	16	26	41	88	164	...	225	760	171	384.7	Over
	120	5	10	15	25	49	92	171	...	226	770	169	420	Over
	180	5	10	16	35	45	79	158	...	220	800	716	458	Over

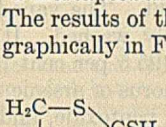


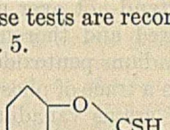


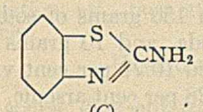
TESTS ON COMPOUNDS SIMILAR TO 1-MERCAPTOBENZOTHIAZOLE

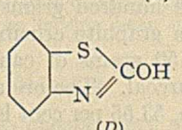
μ-Mercaptothiazoline (*A*), 1-mercaptobenzoxazole (*B*), 1-amidobenzothiazole (*C*), and 1-hydroxybenzothiazole (*D*) were also tested for their accelerating action. Each of these compounds resembles 1-mercaptobenzothiazole in certain parts of its structure. The results of these tests are recorded in Table IV and shown graphically in Fig. 5.


1-MERCAPTOBENZOTHIAZOLE

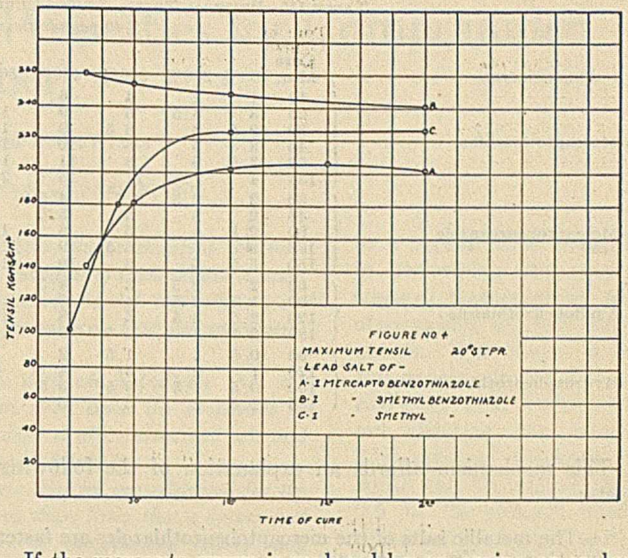

(*A*)


(*B*)


(*C*)


(*D*)

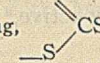
The results show that the μ-mercaptothiazoline exerts a marked accelerating action, but much less than that of 1-mercaptobenzothiazole. This would seem to indicate that the accelerating power is invested in the mercaptothiazole group. When the sulfur atom of the thiazole ring is replaced by oxygen as in 1-mercaptobenzoxazole, the accelerating action is still evident but much lower than that of either 1-mercaptobenzothiazole or μ-mercaptothiazoline.



If the mercapto group is replaced by an amino or an hydroxyl group, as in 1-amidobenzothiazole or 1-hydroxybenzothiazole, respectively, the accelerating action is very greatly diminished; indeed, in the latter substance it is almost entirely absent.

The conclusions to be drawn from these results are as follows:

1—The accelerating action of 1-mercaptobenzothiazole and its derivatives is invested primarily in the mercaptothiazole group. The presence of the benzene nucleus adds markedly to the accelerating value. Whether this is due to the attendant increase in the molecular weight or more directly concerned with the chemical characteristics of the benzene nucleus, is not yet determined.

2—The atomic grouping,  $\underset{-S/}{\overset{\backslash\backslash}{}}CSH$, is directly responsible for the accelerating action. Any change in this grouping either greatly diminishes or completely destroys the accelerating value.

3—The mercapto group is more essential to the acceleration than the sulfur of the thiazole ring, although both are necessary to the best results.

MECHANISM OF ACCELERATION BY MERCAPTOBENZOTHIAZOLE DERIVATIVES

Several theories have recently been advanced to explain the vulcanization of rubber by organic compounds containing the mercapto group. Bruni and Romani[5] have proposed the following mechanism for the acceleration of vulcanization by mercaptobenzothiazoles:

$$\begin{aligned}&2R\text{—}SH + ZnO \longrightarrow (R\text{—}S)_2Zn + H_2O\\&x(R\text{—}S)_2Zn + Sx \longrightarrow xR\text{—}S\text{—}S\text{—}R + xZnS\\&R\text{—}S\text{—}S\text{—}R \longrightarrow R\text{—}S\text{—}R + S\ (\textit{active})\end{aligned}$$

They have lately extended this theory to many other well-known accelerators, such as thiocarbanilide and aldehyde ammonia.[14] It is chiefly interesting as it applies to mercaptobenzothiazole derivatives. The disulfides are less active accelerators than the free mercaptobenzothiazoles, both with and without the presence of zinc oxide. In the absence of zinc oxide both types of derivatives are almost without accelerating power. These facts seem to show that the disulfide cannot be the active agent in this type of acceleration. The theory is therefore inadequate and cannot be accepted.

Bedford and Sebrell[6] have proposed a theory to account for the action of mercapto compounds as accelerators, which may be stated as follows:

$$\begin{aligned}&2R\text{—}SH + ZnO \longrightarrow (R\text{—}S)_2Zn + H_2O\\&(R\text{—}S)_2Zn + S_x \longrightarrow (R\text{—}SS_x)_2Zn\\&(R\text{—}SS_x)_2Zn \longrightarrow (R\text{—}S)_2Zn + S\ (\textit{active})\end{aligned}$$

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[14] Romani, *Caoutchouc gutta-percha*, **19**, 11626 (1922).

TABLE IV—PHYSICAL TESTS: STOCKS CURED WITH ANALOGS OF MERCAPTOBENZOTHIAZOLE

40 pounds steam pressure (141° C.)

ACCELERATOR	Time of Cure Min.	100%	200%	300%	400%	500%	600%	700%	800%	Bk.	Elong.	Tensile Product	Energy of Resilience	STATE OF CURE
μ-Mercaptothiazoline	10	1	2	4	6	8.5	10	20	34	66	900	59.4	68.5	Under
	20	3	4.5	6	9	14	19	35	66	92	895	82.3	197.5	Under
	30	2.5	5	6.5	9	14	23	45	85	108	870	94.0	215	Fair
	45	3.5	5	8	10	14	24	50	95	109	845	92	207.9	Fair
	60	3.5	5	8	11	16	28	48	96	104	825	86	192.5	Slightly over
	135	4	7.5	11	15	23	41	86	..	138	785	108	239.7	Over
1-Mercaptobenzoxazole	30	2	2.5	3.5	4.5	5.5	7	9	14	43	990	42.5	66.6	Under
	45	2	3	5	5.5	7	10	18	32	76	995	75.5	117.8	Under
	60	2.5	4	5	6	10	14	26	42	81	960	77.5	125.4	Under
	105	3	5	6.5	9	12	19	31	59	104	910	94.5	205.8	...
	150	3.5	5	8	10	14	21.5	35	68	91	875	75	190.6	...
1-Amidobenzothiazole	60	2	2.5	3	4.5	6	9	14	22	28	870	24	69.5	All cures poor
	90	1.5	2.5	4	5	8	11	18	28	46	880	40	93.6	
	120	2.5	3.5	5	8	10	17	27	50	57	825	47	111.4	
	180	2.5	4	5.5	9	14	23	38	..	54	785	42.5	116.1	
1-Hydroxybenzothiazole	90	0.5	1	1.5	2	3	4	..	..	5	620	3	10.9	No cures
	120	1	2	3	4	4.5	6	9	14	16	840	13.5	42.5	
	150	0.5	1.5	2.5	3.5	4.5	6	10	17	26	880	23	54.2	
	180	1.5	2	3	5	8	10	18	30	38	850	32	79.5	

This mechanism affords an explanation of the following facts:

1—The metallic salts of the mercaptobenzothiazoles are faster curing than the free compounds.

2—Both the metallic salts and the free compounds are faster curing than the disulfides, which must first undergo a reduction to the mercaptans before functioning as accelerators.

3—All mercaptobenzothiazoles require the presence of zinc or lead oxides for the development of full accelerating power.

4—The metallic salt of the mercaptan is therefore assumed to be the active agent. Excess metallic oxide must be present at all times to reform the salt if it should be decomposed by the action of heat or hydrogen sulfide. Evidence of such decomposition is to be found in the low curing power of these salts in the absence of metallic oxides, and their superior power when an excess of the oxide is present.

While it cannot be shown that sulfur split off from polysulfides is an active form, it has been proved that the sulfur in trithio-oxone is particularly active,[6] and it is inferred that the sulfur yielded by the decomposition of the polysulfides is similarly active.

The polysulfide theory, as given above, appears to offer the best explanation of the existing facts. Doubtless, both the mechanisms given above function in specific cases. It is also probable that no simple explanation of activation will be found which is equally applicable to all types of accelerators. Further work is being done to determine the validity of each of the reactions involved in the above mechanisms.

ACKNOWLEDGMENT

The authors wish to acknowledge the coöperation of the Goodyear Tire & Rubber Company as expressed through E. B. Spear, former research director, for the loan of apparatus and the testing of samples. Further acknowledgment is due C. W. Bedford for helpful advice during the early part of the work, W. J. Kelly for valued suggestions, and C. M. Carson for assistance rendered.

Separation of Arsenic and Phosphorus from Vanadium[1]

By H. A. Doerner

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ARSENIC and phosphorus are frequently found in vanadium ores, especially those of the vanadate type, such as vanadinite. Since vanadium ores and intermediate products containing even small amounts of these impurities are not salable, tests were made to establish a commercially feasible method of separation.

It was found that vanadic acid could be precipitated from an acidified vanadate solution containing arsenic and phosphorus. The latter remain in solution and the precipitate may be washed free from these impurities. Further, a vanadate ore containing arsenic and phosphorus may be treated by the method recommended by the Bureau of Mines.[2] The product will be free from these impurities.

EXPERIMENTAL

1—Twenty-six grams of vanadium oxide, 0.85 gram of arsenic trioxide, and 4.38 grams of sodium ammonium phosphate were dissolved in sodium hydroxide solution, oxidized with sodium peroxide, and acidified with sulfuric acid. The solution was diluted to a volume of 1 liter and sulfuric acid was added until the free acid was 0.05 normal in strength as determined by titration with methyl orange. The solution was boiled with live steam for several hours and allowed to stand hot over night. The vanadic acid precipitate was filtered and thoroughly washed. It contained 24.8 grams vanadium pentoxide (95.5 per cent recovery) and not more than a trace of phosphorus or arsenic. The filtrate contained 1.17 grams vanadium pentoxide, and gave a heavy precipitate with magnesia mixture which contained the arsenic and phosphorus.

2—Five hundred grams of a vanadinite concentrate were fused in a graphite crucible with 150 grams of sodium carbonate, 150 grams of caustic soda, and 10 grams of powdered charcoal. The ore analyzed 10.24 per cent vanadium pentoxide, 53.55 per cent lead, 0.28 per cent arsenic, and 0.27 per cent phosphorus. A lead button of 255.0 grams was obtained. The slag was extracted with hot water in a small pebble mill, filtered, and washed. The solution was treated exactly as described in the first experiment except the volume was 2 liters and the separation was completed as before. The residue from, or the undissolved part of, the slag weighed 203 grams, and contained 0.27 vanadium pentoxide, and much of the phosphorus. The net recovery of vanadium pentoxide was 97.2 per cent free from arsenic or phosphorus.

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[1] Received September 19, 1923. Published with permission of the Director, U. S. Bureau of Mines.

[2] "Metallurgical Possibilities of the Descloizite Ores at Goodsprings, Nev.," *Report of Investigations* **2433**.

Poisson's Ratio and Related Properties for Compounded Rubber[1]

By W. W. Vogt and R. D. Evans

The Goodyear Tire & Rubber Co., Akron, Ohio

The structure of compounded rubber, the mechanical relations of the rubber and filler phases, and the effect of these relations upon the physical properties of the compound, furnish the rubber technologist with a most fruitful and stimulating field for speculative reasoning.

The authors have presented new data which indicate that the shape of the filler particles has an effect upon the properties of Poisson's ratio, volume increase under strain, permanent set, and the stress-strain behavior of compounded rubber.

Explanations of the cause of these changes are advanced for the purpose of stimulating thought along these lines, that a deeper and clearer conception of the structure of compounded rubber may result.

In the course of some studies on the volume increase of compounded rubber when strained, which studies involved the calculations of the volume from simultaneous readings of length, width, and thickness, it soon became apparent that certain stocks behave decidedly different than others. The point of dissimilarity is that for certain stocks the ratio of thickness to width is a constant, while for others it decreases as the strain increases. This evidence of anisotropy requires that the values for Poisson's ratio in the two directions perpendicular to each other must be unequal.

Furthermore, as the stresses developed perpendicular to each other and to the direction of elongation must, from considerations of the symmetry of forces, be equal, then the fact that different strains are produced by these equal stresses proves that there is a dissimilarity of modulus in the two directions.

Since the various stocks studied differ from each other only in the composition of the filler content, it is evident that the exceptional behavior noted is a function of some property of the filler, and the immediate assumption is that the shape or crystal habit of the particles is the determining factor. It is the purpose of this paper to show the effect of particle shape on the physical behavior of compounded rubber with special reference to the properties of Poisson's ratio, volume increase, set, and the stress-strain relations.

Historical

Whitby[2] gives an admirable resumé and critique of the existing data, and mentions specifically the work of Schiller in which evidence is given to show that the value for P is not the same in different directions.

The "dark Para rubber" sheet used gave values of 0.535 and 0.463 in two directions perpendicular to each other. Schippel[3] calls attention to the fact that the average value for P in the case of a highly compounded barytes stock at the breaking elongation was 0.39. This low value was due to the large increase of volume of the stock, the value presumably having been calculated from density measurements.

The other published data are concerned chiefly with the various methods of determining P experimentally, the proper method of calculation, etc., pure gum stocks having been used almost exclusively.

Experimental Method

Test strips, died out from large sheets, were mounted in a suitable stretching frame, by which any desired elongation could be maintained. The width and thickness were measured, with an accuracy of 0.1 per cent, by a traveling microscope and a gage. It was found necessary to adhere closely to a regular time schedule in performing the several steps of manipulation and observation at each elongation. The shape of the test specimens can be varied over wide limits without affecting the results. The ratio of thickness to width can be varied from 2.5 to 25 without effect, provided the length of the specimens is about twenty times the width. These methods, within the limit of accuracy specified, were entirely satisfactory. As a matter of fact, study of different test pieces cut from the same sheet showed that they differed from each other by such amounts that any higher experimental accuracy would be nonsignificant.

Calculation of Poisson's Ratio

This property is defined as the ratio of the percentage of lateral shrinkage of a rod to the corresponding percentage of longitudinal increase, when such increase is infinitesimally small—that is, if we call L the longitudinal and S the lateral dimension,

$$P = \frac{\frac{dS}{S}}{\frac{dL}{L}} = \frac{dS}{dL}\cdot\frac{L}{S}$$

A graphical method of determining dS/dL was found convenient. The corresponding reading of S and L was plotted and a smooth curve was drawn. The value of the tangent to this curve at each desired point gave directly the value of dS/dL, and hence that of P. This definition of P is to be distinguished carefully from that involving finite changes of S and L. This calculation was applied separately to each of the two lateral dimensions, hereafter spoken of as width and thickness. The following symbols will be used to identify the various values:

P_v = value from volumetric measurements
P_t = value in thickness direction
P_w = value in width direction

It is also possible to calculate an average P_v from the change of volume measurements. If each lateral dimension is considered to have the same value and behavior, the expression for volume becomes

$$V = L.S^2$$

Differentiating,

$$dV = S^2.dL + 2SL.dS$$

$$\frac{dV}{dL} = S^2 - 2SL\cdot\frac{dS}{dL}$$

$$= S^2\left(1 - 2\,\frac{L}{S}\cdot\frac{dS}{dL}\right)$$

which becomes, from the definition of P,

$$\frac{dV}{dL} = S^2\,(1 - 2P)$$

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[1] Presented before the Division of Rubber Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] "Plantation Rubber and the Testing of Rubber," p. 486.

[3] This Journal, 12, 33 (1920).

Hence,

$$P = 1/2\left(1 - \frac{1}{S^2}\cdot\frac{dV}{dL}\right)$$

If, further, at each desired elongation, V, L, and S are measured in such units that their instantaneous values are each unity, this becomes

$$P = 1/2\left(1 - \frac{dV}{dL}\right)$$

By plotting V against L, this average P can be computed, using the graphical method for determining dV/dL mentioned above.

The values of P_v calculated by this method were in excellent agreement with the arithmetical average of P_t and P_w as required by the principles of mechanics.

Experimental Data

The results show that the common compounding ingredients may be divided into two classes—those which the writers call "anisotropic," which cause anisotropy of properties in the stocks in which they are compounded, such as graphite, mica, tripoli, clay, light magnesium carbonate, and, strangely enough, glue. The other class, which the writers have called "isotropic pigments," do not exhibit these tendencies, and include gas black, lampblack, iron oxide, zinc oxide, lithopone, and barytes.

Thickness-Width Ratio—The first criterion which was used in classing the pigments was called the thickness-width ratio. If the reading of thickness is divided by the corresponding reading of width as the test pieces are progressively strained, the values obtained constantly decrease for the anisotropic fillers, and remain constant for the isotropic class. The writers have recalculated all values of T/W in such a manner that the value T/W at 0 per cent elongation becomes 1.0.

The data shown in Fig. 1 were obtained on stocks containing 20 volumes of filler per 100 volumes of rubber, cured to the correct technical cure.

The stocks were milled on small (6 × 12 inches) rolls in such a manner as to "set the grain"—i. e., align the pigment particles—were allowed to age 1 hour on a warming table to permit readjustment of internal strains in the rubber phase, and then 24 hours at room temperature, after which they were cured in molds, using enough stock to give a perfect sheet with a small overflow (5 per cent). Unless otherwise noted, all test pieces were died out in the direction of the grain.

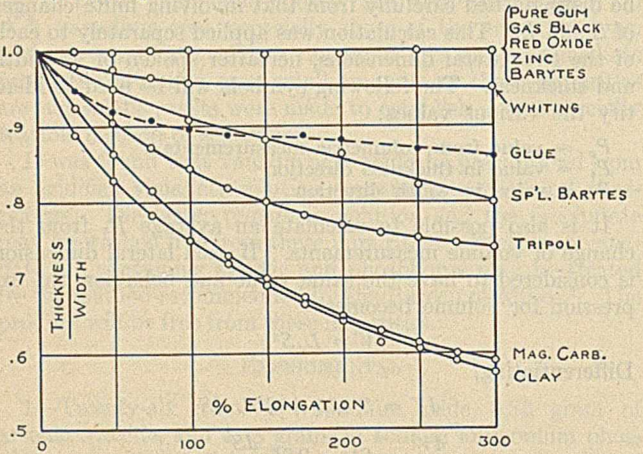

Fig. 1

Poisson's Ratio—The T/W ratio is a criterion which is easily obtained experimentally and can be calculated and interpreted readily. However, Poisson's ratio is a recognized absolute property, and was therefore specifically calculated in all cases.

In considering the value of Poisson's ratio, the following cases must be considered:

When the volume of the rubber under strain remains constant, we have two cases:

(1) $P_w = P_t = 0.5$

(2) P_w does not equal P_t, but $\frac{P_w + P_t}{2} = 0.5$

When the volume does not remain constant on stretching, we may have

(3) $P_w = P_t < 0.5$

(4) P_w does not equal P_t, and $\frac{P_w + P_t}{2} < 0.5$

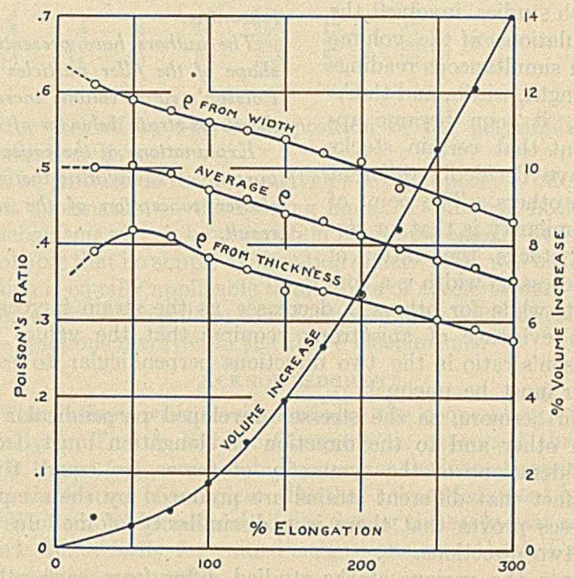

Fig. 2

Case 1—All isotropic pigments studied fulfil Case 1 at low elongations (25 per cent), because the volume changes are practically negligible. Such fillers as gas black and zinc oxide fulfil the conditions up to elongations of 200 per cent, there being practically no increase of volume at this elongation. The values for P_t and P_w are both 0.5.

Case 2—The values for P_t and P_w for some typical anisotropic pigments at 25 per cent elongation are given in the following table:

Table I

Pigment	P_t	P_w	$\frac{P_t + P_w}{2}$
Magnesium carbonate	0.72	0.30	0.51
Clay	0.69	0.32	0.505
Tripoli	0.61	0.39	0.50
Special barytes	0.57	0.42	0.50

Case 3—This case is illustrated by barytes, lithopone, and other isotropic pigments at high elongations, say 300 per cent, where there is a considerable increase in volume.

Case 4—This is illustrated very neatly by tripoli, an anisotropic filler which gives large volume increases at high elongations. This behavior is represented graphically in Fig. 2. The volume increase curve is also given.

It will be readily appreciated that for low elongations the graph shows the behavior as given under Case 2, while for the higher elongations the conditions fulfil Case 4.

Stress-Strain Relations in Different Directions—As had been stated above, stocks compounded with anisotropic pigments should give different stress-strain relations in different directions. Therefore, a stock containing 20 volumes of clay per 100 volumes of rubber was so prepared that stress-strain curves might be obtained, the tests being taken with the grain, across the grain, and vertical to the grain (perpendicular to the plane of the calender). The preparation of the last-mentioned test piece is rather difficult, the alignment of filler particles probably being quite badly disarranged during the process. However, the tests were obtained, particular care being exercised to secure identical curing conditions. The results are shown graphically in Fig. 3.

Additional properties of these three stocks were determined as follows:

TABLE II

	Volume Increase at 250% %	*T/W* at 250% Elongation %	Permanent Set %
With grain	4.4	0.76	44
Across grain	5.5	0.69	36
Vertical to grain	8.1	0.74	30

PERMANENT SET

Values for permanent set for stocks compounded with 20 volumes of filler per 100 volumes of rubber are given in the following table:

TABLE III

	PIGMENT	PERMANENT SET %
ANISOTROPIC FILLERS	Magnesium carbonate	52
	Clay	44
	Special barytes	32
	Tripoli	29
ISOTROPIC FILLERS	Gas black	33
	Zinc oxide	23
	Red oxide	22
	Lithopone	20
	Whiting	15
	Barytes	14
	Pure gum	6

A comparison of the properties of ordinary and the special barytes brings out strikingly that particle shape, rather than such factors as degree of fineness, surface activity, selective wetting, or adsorption, is the fundamental cause of these abnormal properties. The special barytes was made by such a process that it consists almost entirely of long, flat plates and needles, whereas the regular barytes was the commercial ground product, consisting of broken fragments of no regular geometric shape. The samples were closely alike as regards average particle size and were compounded on the basis of 20 volumes of pigment per 100 volumes of rubber. The values for *T/W* ratio, Poisson's ratio, and permanent set are given below.

TABLE IV

	T/W Ratio at 200% Elongation	P_t	P_w	$\frac{P_t + P_w}{2}$	Permanent Set %
Regular barytes	1.00	0.50	0.50	0.50	14
Special barytes	0.86	0.57	0.42	0.50	32

The stress-strain relationships (taken with the grain at the correct technical cure) furnish additional evidence of differences between the isotropic and anisotropic fillers.

TABLE V

	100%	300%	500%	Tensile Kg./Sq. Cm.	Elongation %
Regular barytes	7	17	42	132	700
Special barytes	18	42	91	160	640

The four properties mentioned above are dependent to a greater or less degree upon crystal habit, but it is believed that Poisson's ratio and the *T/W* ratio are almost wholly dependent on this characteristic.

LAMINATION EFFECTS OF THE CURED STOCK

The ability to separate the cured sheet into layers in the same manner as a sheet of mica may be split is another criterion which may be used to demonstrate anisotropy. The pigments that give stocks which laminate are mica, graphite, clay, magnesium carbonate, tripoli, and the special barytes. Here again the differences between the special and regular barytes are especially striking. It will be recognized that these fillers are without exception classed as anisotropic by other methods.

VEILS

The familiar silky appearance of the precipitate which forms on adding mercuric chloride to a solution of stannous chloride, or that due to a suspension of bismuth subnitrate or vanadium pentoxide in water, has been directly proved to be caused by the needle or tabular shape of the solid particles, and Freundlich[4] has developed a method for determining crystal habit based upon the changes in the strength of the Tyndall beam, depending upon the plane of observation with respect to the alignment of the particles. The presence of this "veil" (German word is "Schlierenbildung," meaning veil formation) is a qualitative test for anisotropy of shape.

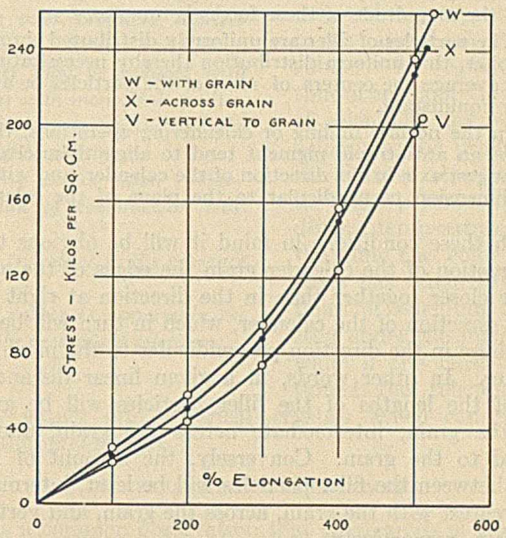

FIG. 3

If a dilute suspension of the pigment is made in water, preferably with gum arabic as a protective colloid, agitation of the suspension will reveal the presence of veils only in the case of anisotropic pigments. Mica furnishes a very excellent example of this effect. The size of the particles of pigment will probably have some influence upon the phenomenon, so it would not be absolutely proved that a pigment which does not show the effect is isotropic. However, all the pigments which by other means have been classed as anisotropic give veils, whereas none of the isotropic pigments give the effect.

The differences between the special and regular barytes, which have been noted by the other methods, are strikingly revealed by this test.

DISCUSSION OF RESULTS

The experimental results given above were obtained on stocks which were so prepared as to suppress the grain effects due to the rubber phase and to accentuate the effects due to the filler phase so far as this is possible. With this point clearly in mind, the evidence is positive that the shape of the filler is a major contributing cause of the changes in the properties of the stocks. The questions to be answered therefore are:

1—What shape is necessary to explain these effects?

2—What is the mechanism of the action by which these effects are produced?

In view of the known facts that the particle shape of mica, graphite, special barytes is tablets or placques, and that tripoli contains a large percentage of tabular diatoms, the writers are justified in saying that any shape wherein

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[4] *Physik. Z.*, **17**, 117 (1916).

any two dimensions are considerably greater than the third will explain the effects observed.

In answer to the second question as to the mechanism, the following reasoning is advanced in explanation of the facts. The following conditions are postulated:

1—There is a union between the particles of filler and the rubber, which bond may be chemical union, physical adsorption, surface friction, or mechanical interlocking. An estimation of the magnitude of these forces is unnecessary.

2—The particles of filler are uniformly distributed throughout the rubber, this uniform distribution thereby necessitating that on the average the centers of mass of the particles be approximately equidistant.

3—In the normal milling or calendering operations, the particles of an anisotropic pigment tend to align themselves with their longest axis in the direction of the calender, and with their least dimension perpendicular to the plane of the calender.

With these conditions in mind it will be obvious that in the direction of the calender grain the edges of the crystals will be closer together than in the direction at right angles to the direction of the calender, which in turn will be closer than those in the direction perpendicular to the plane of the calender. In other words, in a given linear distance, the sum of the lengths of the filler particles will be greatest with the grain, intermediate across the grain, and least vertical to the grain. Conversely, the amount of rubber phase between the filler particles will be least, intermediate, and greatest with the grain, across the grain, and vertical to the grain, respectively.

Consequently, to effect a given elongation in any direction, inasmuch as the pigment phase does not elongate, the rubber must be stretched to such a point as will give the total elongation desired. It is therefore evident that the lesser amount of rubber will have to be elongated to a greater proportion of its ultimate elongation. This means that a higher stress must be imposed. This, then, is the reason why a stock compounded with an anisotropic filler has a stiffer stress-strain curve with the grain. The stress-strain across the grain may be equal to or softer than the "with grain" curve (depending on the ratio of the length to width dimensions of the particular filler), but both will be stiffer than the "vertical to grain" curve.

Referring to the values of permanent set given in Table III, it is found that, within each class of pigments, the permanent set is greater the smaller the particle size. That is, permanent set increases with increase of filler surface, and this fact lends weight to the argument that permanent set is in part due to a dislodgment of rubber and pigment surfaces, which, having been cured up in contact with each other, on removal of the stretching force experience frictional difficulty or even definite obstruction in becoming readjusted to their original condition of fit. Since anisotropic particles have more surface per unit volume than isotropic particles of the same average bulk, for this reason alone they might be expected to show greater permanent set.

Furthermore, for anisotropic pigments the greatest amount of rubber-pigment interface will be involved in this dislocation under strain when that strain is parallel to the longest dimension of the pigment—that is, with the grain—intermediate in value when the strain is across the grain, and least when the strain is vertical to the grain. Hence, we should expect the permanent set for the stocks referred to in Table II to be greatest for the "with grain" stock, intermediate for the "across grain" stock, and least for the "vertical to grain" stock. Permanent-set measurements on these three stocks gave, respectively, 44, 36, and 30 per cent.

Mention is made above of the volume increases which occur when the stock is subjected to strain in the three different directions. Schippel has shown that the per cent increase in volume is largely a direct function of the area of the particle in a plane normal to the strain lines. The areas so defined and therefore the values of volume increase, in the case of these clay stocks, will be least, intermediate, and greatest, for strains in a direction with the grain, across the grain, and vertical to the grain, respectively. The values found were 4.4, 5.5, and 8.1 per cent.

The *T/W* ratios obtained when the direction of strain is always parallel to the length of the test piece, but where the length of the test piece itself is with the grain, across the grain or vertical to the grain, furnish a fascinating subject for speculative analysis.

By an extension of the reasoning used in developing the explanation for the difference in stress-strain behavior, in a qualitative way, at least, the causes for the variation in *T/W* ratios in different directions can be explained.

Thus, when a strain is imposed parallel to the grain, considerations of symmetry require that the contractive stresses in the two lateral directions must be equal. Since, however, as has been outlined above, the percentages of rubber phase in a given linear distance are unequal in the widthwise and thickwise dimensions, the imposition of equal stresses will cause equal strains to be set up in the rubber phase but unequal total contractions of the material as a whole, since the pigment phase is rigid.

The exact quantitative differences in the *T/W* ratio in different directions depend on relative magnitudes of the average ratios of each pair of dimensions of the pigment particles, assuming that the particles are perfectly uniform in shape, size, distribution, and orientation, a condition which is well-nigh experimentally impossible.

The *T/W* ratios given in Table IV are explainable on the basis that the length, width, and thickness dimensions of the typical clay particle are approximately as 5 : 2 : 1.

The explanation of the lamination effects observed with typical anisotropic fillers probably is that the bond between the filler surface and the rubber is less than the tensile of the rubber itself. Therefore, instead of the rubber tearing within itself in a haphazard, irregular direction, it separates from the broad faces of the filler particles. The line of cleavage is thus defined by the alignment of the filler particles and lamination ensues.

These explanations of the experimental facts justify the hypothesis advanced and may possibly give a clearer conception of the structure of compounded rubber and of the effect of the filler phase upon some of the properties of this material with particular reference to its anisotropy.

M. Carey Lea—Chemist

America's contributions to chemistry have been the theme of years of study by Edgar F. Smith, and through the publication of these studies he has done more than any other one man to put the facts of these discoveries and discoverers before American chemists. The latest work from his kindly pen is entitled "M. Carey Lea—Chemist."

Lea (1823–1897) was a student under J. C. Booth in his famous teaching laboratory, after having studied law and having been admitted to the bar. His studies after leaving Dr. Booth's laboratory were largely carried out in his private laboratory in his home in Philadelphia. His most important investigations dealt with picric acid and the picrates, the Pennsylvania coal seams, the metals of the platinum group, and photography. His work on photography was decidedly his most important contribution to knowledge. His only book, "Photography," went through two editions and was extremely popular with the devotees of this new art at the time. Lea was a recluse and was known personally to few of his contemporaries. His work was published in the *American Journal of Science* from 1858 to 1897, and *Chemical News*, 1862, contains four contributions from his laboratory.

The present story of his life is published privately by the author in a 12-page pamphlet with an engraving of the subject.

Selenium in Rubber Compounding[1]

By Ira Williams

Firestone Tire & Rubber Co., Akron, Ohio

Selenium may be introduced into rubber by the addition of fused mixtures of sulfur and selenium. The color produced changes from yellow to red as the size of the particles of selenium increases.

The crystallization of sulfur in rubber may be induced with selenium because selenium is isomorphous with monoclinic sulfur. In this way metastable solutions of sulfur are prevented and the initial rapid bloom of uncured stocks may be eliminated.

Selenium exerts a distinct accelerating action upon rubber-sulfur mixtures, while the actual amount of combination with selenium is small.

Selenium alone will produce some cure in rubber in the presence of an organic accelerator.

The acetone extract of resin from the rubber is apparently reduced when vulcanization is carried out in the presence of selenium.

IT IS to be expected from the chemical analogy between oxygen, sulfur, selenium, and tellurium, that any of these would produce vulcanization in a rubber compound. Probably the most important of these, other than sulfur, is selenium, and it has been shown by Boggs[2] that selenium may be used as a vulcanizing agent. It is possible that the effectiveness of these materials in the vulcanization process will depend somewhat on the effective concentration of the material in the rubber. While sulfur is quite soluble in rubber, tellurium is insoluble. The best figures which have been obtained in the present work place the solubility of selenium at less than 0.05 per cent at 80° C. Oxygen is somewhat more soluble, and it is known that cures may be obtained by means of oxygen without the presence of sulfur. In the case of sulfur the effective concentration may be very much increased at temperatures above its melting point, but in the case of both selenium and tellurium it is impossible to reach their melting points (217° and 451° C., respectively) without producing decomposition in the rubber. If the effectiveness of these elements in producing vulcanization of rubber is judged by the possible molar concentration, the elements would then be placed in the order—sulfur, oxygen, selenium, tellurium. This order might be affected if a higher concentration could be produced by such means as introducing the element in an adsorbed condition or in a finer state of division.

Sulfur and selenium are miscible in the fused state in all proportions, and form a eutectic mixture which melts at 106° C. and contains 40 atomic per cent of sulfur. Mixtures of this kind crystallize very slowly, and immediately after fusion may be milled into rubber to form a master batch which will keep for an indefinite period. In this manner mixtures of sulfur and selenium containing as high as 70 per cent of selenium may be prepared and held in rubber for use in compounding. While selenium may be used without first fusing with sulfur, the equilibrium of the system will be reached quite slowly, especially at low temperatures, and the same distribution of selenium cannot be obtained.

Color in Selenium Stocks

The colors obtained by introducing a fused mixture of sulfur and selenium into rubber are produced by the distribution of sulfur between the rubber and selenium. In this manner colloidal selenium is formed. The uncured stock varies from a bright yellow, when little selenium is present in a very fine colloidal state, to a deep orange color when more selenium is used. Upon curing, the size of the colloidal particle slowly increases and the color changes from yellow through orange, deep red, brown, and finally to the natural color of cured rubber. By regulating the time of cure and the amount of selenium, any of these colors may be produced in the finished stock and will be quite permanent at ordinary temperatures. By the time the color of the stock has reached red, particles of selenium may be seen under the microscope, while if the cure is continued the selenium will finally gather into spherical crystals which can be seen with the unaided eye.

Crystallization Phenomena

It is a common observation that compounds of low sulfur content bloom very easily while in the uncured state. This is due to the fact that the temperature reached during the milling period is sufficient to cause all the sulfur to go into solution. Upon cooling, the system becomes metastable because the rubber is supersaturated with sulfur. When the surface of such a stock is touched, crystallization occurs at that point, and these crystals serve as nuclei for the growth of the large crystals which quickly appear as bloom.

Metallic selenium, because of its being isomorphous with monoclinic sulfur, may be used to prevent the formation of a supersaturated solution of sulfur. If 0.05 or 0.10 per cent of finely divided selenium is milled into the stock, each particle of selenium, which owing to its low solubility and the slow rate at which equilibrium is established at low temperatures, becomes a center for the crystallization of sulfur. After crystallization has taken place a disturbance will not produce bloom, and the condition known in the industry as "dry stock" may in this way be quite effectively avoided. In a pure gum stock this crystallization requires from 10 to 15 minutes, but since crystallization is slower in the presence of a large volume of filler, it is necessary to produce more centers of crystallization by using a larger quantity of selenium.

Experimental

As a control for a study of the effect of selenium on cure, a simple rubber-sulfur mixture was used. Replacement of part of the sulfur by selenium was done on a molecular basis. In each of the following compounds the sum of sulfur and selenium is equivalent to 6 per cent of sulfur to the rubber.

Stock	Pale Crepe G.	Sulfur G.	Selenium G.
47	94.00	6.00	0.00
48	94.00	5.11	2.19
49	94.00	4.51	3.69
50	94.00	3.73	5.60
51	94.00	0.00	14.80

These stocks were cured at 290° F. in an oil bath which controlled the temperature to ± 0.5° C. The physical properties of all, with the exception of Stock 51, which showed no signs of cure after 5 hours, are plotted in Fig. 1. In such

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[1] Presented before the Division of Rubber Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] This Journal, **10**, 117 (1918).

a diagram the rate of cure (not to be confused with time of "optimum" cure), as measured by the rate of change in stiffness of the stock, can be judged by the slope of the first part of the curve. The addition of selenium has produced an increased rate of cure in all compounds containing sulfur. Stock 48, which contains only 2.17 per cent of selenium, cures at approximately twice the rate of the simple rubber-sulfur mixture. After this the addition of selenium at the expense of sulfur causes a decrease in the rate of cure until finally a stock which does not cure at all results.

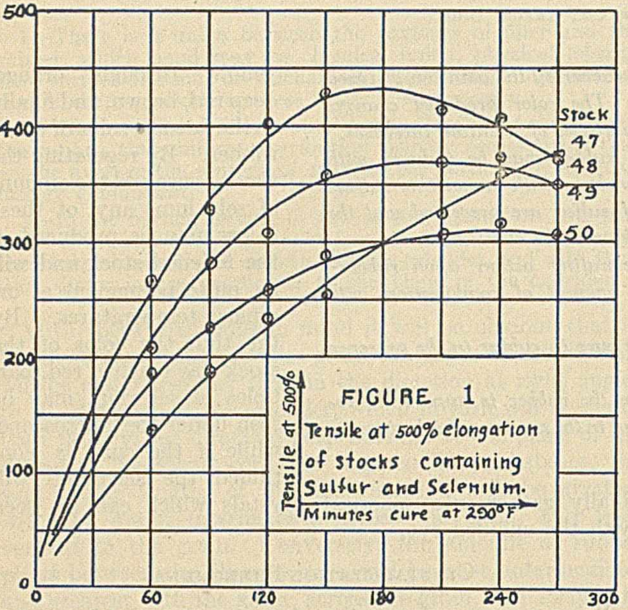


FIGURE 1
Tensile at 500% elongation of stocks containing Sulfur and Selenium.

There are at least two possible factors which influence the rate of cure of these stocks.

(1) The solubility of the selenium may be increased until it becomes an effective vulcanizing agent.
(2) The selenium may act simply as an accelerator.

The mixture of sulfur and selenium having the lowest melting point contains 62 per cent by weight of selenium. Stock 48, which shows the highest rate of cure, contains only 30 per cent by weight of selenium in the sulfur-selenium mixture, but since the selenium is very slightly soluble in the rubber, the distribution of sulfur between the rubber and the selenium may be such that the eutectic mixture of sulfur and selenium is approached. Further addition of selenium and reduction of sulfur would then result in a higher melting point and reduced vulcanizing properties. This is probably true if selenium functions in the same manner as sulfur, but does not necessarily follow if the selenium acts merely as an accelerator. That selenium does act as an accelerator is indicated by the curves in Fig. 1, since the addition of only a small amount of selenium has greatly increased the rate of cure, while the selenium alone produced no cure. After the addition of selenium the decrease in sulfur has retarded cure in a manner similar to that experienced when the sulfur is reduced in the presence of an organic accelerator. The accelerating action (in per cent) is shown further by the following stocks, in which a small amount of selenium has been added to a compound already containing an organic accelerator:

Stock	Rubber	Sulfur	Zinc Oxide	Aldehyde Ammonia	Selenium
52	93.00	3.00	3.00	1.00	0.00
53	92.80	3.00	3.00	1.00	0.20

The physical properties of these compounds are shown in Fig. 2. Both the rate of cure and stiffness of the rubber have been increased much more than they would have been by the addition of either the same amount of aldehyde ammonia or sulfur. This indicates either a marked activity as an accelerator or a specific action of selenium which is produced by neither accelerator nor sulfur.

Neither of these explanations is in itself sufficient to explain the action of selenium, because, as pointed out by Boggs, selenium is capable of producing a cure at the temperature employed if an organic accelerator is added. A stock containing 70 per cent of rubber and 30 per cent of selenium showed no cure after 5 hours at 290° F. The same stock with 2 per cent of rubber replaced by 1 per cent of zinc oxide and 1 per cent of aldehyde ammonia gave a tensile of 1300 pounds after 30 minutes' cure. The stiffness and strength slowly decreased upon longer cures until it reached a tensile of only 900 pounds after 4 hours. This behavior is distinctly different from that of a rubber mix containing such a high percentage of sulfur, in which case the stiffness would have continued to increase.

ANALYSIS OF STOCKS CONTAINING SELENIUM

The determination of the chemical properties is accomplished with difficulty because of the presence of both selenium and sulfur. It is possible by means of an ordinary acetone extraction to remove some selenium. Bloom which occurs on undercured sulfur-selenium stocks is composed of both sulfur and selenium, so that the mixed crystals of sulfur and selenium are somewhat soluble in rubber and may be extracted. Further extraction of selenium after the free sulfur has been removed is extremely slow. The extraction is made all the more difficult by the fact that selenium, which is heated even to temperatures as low as 100° C., tends to assume the more insoluble form. It is possible that repeated addition of sulfur to the stock with repeated extractions might be a means of removing all free selenium. Crystals were found in Stock 48 after curing for 60, 90, or 120 minutes. Small strips, each 0.02 inch in thickness, were placed in a Soxhlet apparatus and extracted with acetone. Although the 60-minute cure contained the most crystals, all had disappeared after 2 hours of extraction. Those in the 90-minute cure had practically disappeared after 6 hours, while the 120-minute cure had apparently not changed after 2 days. A microscopic examination revealed the fact that, while the crystals were once well formed, they had been reduced during the

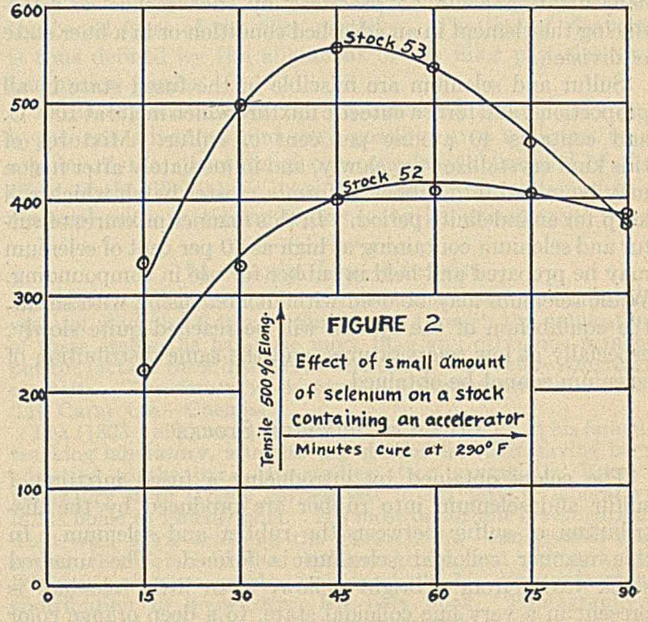


FIGURE 2
Effect of small amount of selenium on a stock containing an accelerator

extraction to a series of broken points which, without magnification, still showed the original outline. These changes again point to the fact that free sulfur is necessary for the successful extraction of selenium.

Microscopic examination was made of sections of sulfur-selenium stocks which were cured to the point where practically no free sulfur remained. The amount of selenium present was estimated by counting and measuring the particles, and, within the limits of accuracy of this method, all the selenium could be accounted for. This showed that the amount of combined selenium must be small and is not to be compared in magnitude with the amount of combined sulfur. No further efforts were made to determine combined selenium.


FIGURE 3

Combined sulfur and extraction loss of stocks containing sulfur and selenium

Mixtures of sulfuric and selenic acid may be separated in acid solution by the addition of potassium iodide. The iodine may then be titrated with standard arsenite and the selenium determined, after which the sulfate may be precipitated. This method cannot be used if a nitrate fusion has been used in the oxidation of the sulfur and selenium, unless the nitrate and nitrites are first removed. If the selenium is not to be determined it may be reduced in the presence of a nitrate, but the presence of nitrites, which are always produced during the fusion, prevents the precipitation of selenium. This precipitation is, however, easily accomplished in acid solution by either sulfites or stannous chloride. Combined sulfur was finally determined after removal of selenium by the addition of the calculated amount of stannous chloride. The following check determinations were made by this method on a stock of known sulfur and selenium content:

Sulfur Present G.	Selenium Present G.	Sulfur Found G.
0.0163	0.0103	0.0162
0.0163	0.0103	0.0159
0.0163	0.0103	0.0167
0.0163	0.0103	0.0169

In Fig. 3 are shown the values for combined sulfur and for extraction loss of Stocks 47, 48, and 49. In all stocks containing selenium, the same stiffness is reached with lower combined sulfur. This resembles the action of stocks containing an organic accelerator. The extraction loss of the rubber–sulfur mixture reaches a minimum of 3.3 per cent at 240 minutes' cure. This is slightly more than the normal resin content of the rubber. In all the selenium stocks a minimum extract of only slightly more than 1.5 per cent is found. This is approximately 1.1 per cent below the original resin content of the rubber.

Although selenium alone or with an accelerator is somewhat effective as a vulcanizing agent, it is apparent that it functions chiefly as an accelerator when used with sulfur. All accelerators in common use, whether organic or inorganic, are chemical compounds, but here is a case of the increased action being brought about by an element. Complications arising in the study of the accelerators of vulcanization can be greatly reduced by the elimination of many uncertain decomposition products, if selenium is used as the accelerator. The action between accelerator and sulfur is also reduced to a more simple state. It is possible that a study of the action of selenium in rubber will throw more light on the nature of acceleration.

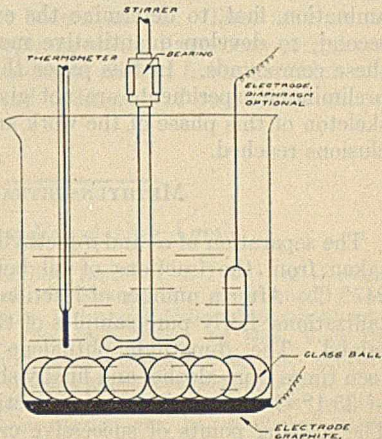
A Ball-Mill Electrolytic Cell[1]

By Alexander Lowy and Alfred R. Ebberts

University of Pittsburgh, Pittsburgh, Pa.

During the course of an investigation in this laboratory of the electrolytic oxidation of anthracene, a novel type of cell was designed and constructed. Certain solids in suspension have a tendency to aggregate under the action of the current. Also, when the superficial layer of any particle has entered into reaction, it prevents or slows up the action on the central portion of the particle. To prevent both of these undesirable effects this cell was designed.

The stirrer was equipped with paddles to produce a swirling motion in the electrolyte, and glass balls were introduced, which were carried rapidly round and round by the swirling liquid. The thermometer and one electrode were raised enough to allow the balls to pass under them. The other electrode was on the bottom of the beaker and a connection for it was sealed in the glass. For large balls several glass marbles, such as children play with, were used, and for small ones the solid beads furnished for Hempel fractionating columns. The size of ball must be determined by conditions. Mercury as electrode has the advantage of not requiring sealing into the cell, and also that no trouble due to solids adhering to the electrode surface is experienced. The solid anodes used by the authors were sealed in place with Redmanol cement, which was found to be very satisfactory. Heat should be supplied by bath only. Direct heating causes the dissolution of the cell due to the different coefficients of expansion of the materials used and the excessive local heating.



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[1] Received September 13, 1923.

Some of the Constituents of Coke-Oven Tar[1]

By John M. Weiss and Charles R. Downs

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THERE is a rather popular idea that anything can be found in coal tar, based on the assumption of the layman that coal-tar products are in general found in tar itself. Even the technical man is under some misapprehension, as Lunge in his book on "Coal Tar and Ammonia" lists some two hundred odd substances which various investigators have claimed to have found in tars from various sources, including such widely differing types as blast furnace, peat, lignite, and wood tars, as well as the various tars from bituminous coal. The type of tar produced in greatest quantity in the United States is coke-oven tar, so it seems that more exact information on its composition is desirable. The past exact knowledge is largely confined to the light oil below 200° C., the tar acids, and the tar bases, all of which are comparatively easy to separate and examine.

The present communication is designed to throw light on the composition of the neutral oils boiling above 200° C., both as to the principal compounds present and their amount. Naturally, a study of the composition of all varieties of American coke-oven tars would be a very long investigation, but the composition of the average coke-oven tar is of interest to show what compounds are commercially available. The results can be accepted with the usual reservations which all conversant with the tar industry make because of the variations in the raw material of the industry. The work described comprises two phases—qualitative and quantitative.

The qualitative test involved a larger sample than chemists are wont to use in their analyses. About 20,000 gallons of coal-tar distillate oil were handled, the tar acids and bases removed by extraction with caustic soda solution and dilute sulfuric acid, and the extracted oil was settled to remove the hydrocarbons crystallizable at normal temperature. This left about 10,000 gallons of neutral settled oil, which was distilled in the most refined type of vacuum column still. The distillate was collected in 100-gallon fractions, and these fractions were taken for the laboratory qualitative examination, first, to determine the existing compounds, and, second, to develop quantitative methods for estimation of these compounds. In this paper the detailed results of the preliminary experiments are not given in full, but rather a skeleton of this phase of the work and the final general conclusions reached.

METHYLNAPHTHALENE

The separation of α- and β-methylnaphthalenes was undertaken from the fractions of oil boiling between 235° and 247° C. After a number of fractional distillations and crystallizations, fairly pure samples of the two isomers were obtained. The β-methylnaphthalene was crystallized fourteen times from alcohol and finally showed a solidifying point of 35.1° C. and an index of refraction at 40° C. of 1.6028. The melting points of successive crops of crystals had not become absolutely constant, but were nearly so.

The α-methylnaphthalene was purified by recrystallizing the picrate and decomposing it. The melting point of the picrate was 123° C. and the index of refraction of the hydrocarbon at 40° C. was 1.5882. There was therefore sufficient difference in the indices of refraction to use this constant as a method of estimation, if only the two isomers were present in a mixture. The constant is seriously depressed by the presence of paraffins in the oils which may amount to 4 per cent. All other impurities, however, can be removed and the paraffins estimated and their effect on the index of refraction calculated from the determined value for their index of refraction at 40° C. of about 1.4316. The writers did not go further into the properties of the monomethylnaphthalenes, as at this point they had sufficient data to enable them to make reasonably approximate estimates of the methylnaphthalene content of oils, and had concluded, further, that in general, with the products investigated, the proportions of α- to β-methylnaphthalene were 1.45 to 1.00.

The fractions containing the methylnaphthalenes were examined for trimethylcoumarones, with negative results. The fractions just above the monomethylnaphthalenes contained dimethylnaphthalenes in complex mixture. No attempt was made to separate the individual isomers, but they were estimated *en masse* by fractional distillation.

DIPHENYL

This body was estimated in several of the fractions by sulfonation at 40° to 50° C. with concentrated sulfuric acid and pouring the sulfonated mass into an excess of water. By extraction with ether, a crude diphenyl was obtained which was purified from admixed paraffin hydrocarbons by crystallization from alcohol. The richest fraction contained only 8 per cent of the crude material, and, based on the original tar, the amounts present were only around 0.1 per cent.

FLUORENE

The fractions in which fluorene should be present were nearly solid and the separated pressed solids were nearly pure material, merely requiring a wash with sulfuric acid and redistillation to remove small amounts of resinifying hydrocarbons.

ACENAPHTHENE

The fractions in this range acted very similarly to the fluorene fractions, and the isolation of acenaphthene was not difficult. The separated liquid oil from acenaphthene, as well as that from fluorene, was not examined very thoroughly, as on redistillation it gave considerably more of the parent hydrocarbon and the actual amounts of true liquid oil were materially lessened.

PHENANTHRENE

The development of a direct method of analysis for phenanthrene in crude solids was a long and tedious task. The method finally perfected involved the formation of phenanthraquinone by oxidation in glacial acetic acid solution with iodic acid and the precipitation of the phenanthraquinone in weighable form by either 1,3,4-toluylenediamine or 1-ethoxy-3,4-diaminobenzene. The details of this form the subject of a paper by Williams.[2] In connection with the

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[1] Presented before the Division of Organic Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] *J. Am. Chem. Soc.*, **43**, 1911 (1921).

work pure phenanthrene was prepared and found to have a melting point of 99.6° C.

MISCELLANEOUS

Naphthalene, anthracene, and carbazol were separated and estimated in the usual way in the solids from their fractions. Diphenylene oxide was sought, with negative results. Above the anthracene oils are obtained the last oils from the distillation of tar which can be roughly separated into yellow solids, greases, and resinous bodies—all of unknown composition and affording fields for further research work. The separation of these products has been described by Bailey and Boettner.[3] The yellow solids have been shown to contain chrysene and picene, and are a rather complicated mixture.

As exemplifying the work, the results obtained on one of the still runs of higher boiling oil are shown graphically in the accompanying curve. Still temperatures are not given, as under a varying vacuum they are of very little value. In the greater portion of the range over 70 per cent of the compounds present were actually definitely determined. The percentages of acenaphthene and fluorene as determined are probably somewhat low and account partly for the drop of the total curve between Fractions 16 and 23. The fractions also vary in paraffin content from 2 to 5 per cent and from 5 to 7 per cent in unsaturated hydrocarbons, but as these have not been determined in all fractions in this set, they were omitted. If included they would bring a considerable portion of the total curve close to 100 per cent. The naphthalene and monomethylnaphthalene end is not characteristic as these had been largely removed by a previous distillation.

CONSTITUENTS OF TAR

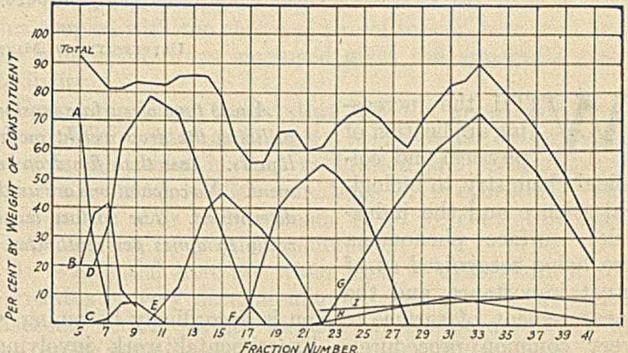
With the data obtained in the preliminary work a new start was made. A mixture of four representative coke-oven tars with a specific gravity at 15.5° C. of 1.186 and a benzene insoluble of 10.6 per cent was selected, and was run first in the plant and then in the laboratory, distillation losses being eliminated by equation as the work proceeded. The net final results are shown in the following table:

CONSTITUENTS OF TAR

	Per cent by Weight on Dry Tar
Light oil:	
Crude benzene and toluene	0.3
Coumarone, indene, etc.	0.6
Xylenes, cumenes, and isomers	1.1
Middle and heavy oils:	
Naphthalene	10.9
Unidentified oils in range of naphthalene and methylnaphthalenes	1.7
α-Monomethylnaphthalene	1.0
β-Monomethylnaphthalene	1.5
Dimethylnaphthalenes	3.4
Acenaphthene	1.4
Unidentified oil in range of acenaphthene	1.0
Fluorene	1.6
Unidentified oil in range of fluorene	1.2
Anthracene oil:	
Phenanthrene	4.0
Anthracene	1.1
Carbazol and kindred nonbasic nitrogen-containing bodies	2.3
Unidentified oils, anthracene range	5.4
Phenol	0.7
Phenol homologs (largely cresols and xylenols)	1.5
Tar bases (mostly pyridine, picolines, lutidines, quinolines, and acridine)	2.3
Yellow solids of pitch oils	0.6
Pitch greases	6.4
Resinous bodies	5.3
Pitch (460° F. melting point)	44.7
TOTAL	100.0

The general composition of the distillate portion of the tar is fairly well accounted for, the unidentified material in the lower ranges being inconsiderable (largely unsaturated hydrocarbons and paraffins or hydro-aromatics), the greater part of the unidentified materials occurring in the oils of the anthracene range and the solids and greases just below the hard pitch.

It is, of course, to be borne in mind that these results represent the composition of a mixture of several coke-oven tars, and other mixtures or single varieties of these might show different percentages of materials, but these variations cannot be estimated at present. The amounts given should not be taken as commercially recoverable, as it would not ordinarily be practicable to refine oils to the extent necessary to obtain all of any given constituent.



A—NAPHTHALENE. B—MONOMETHYLNAPHTHALENES. C—DIPHENYL. D—DIMETHYLNAPHTHALENES. E—ACENAPHTHENE. F—FLUORENE. G—PHENANTHRENE. H—ANTHRACENE. I—CARBAZOL

The most notable feature of the results is the comparatively few compounds existing in the tar in appreciable amount, probably not over one-quarter of those popularly supposed to be there. The fact that phenanthrene is the second most abundant chemical in tar is also surprising and indicates the desirability of work to effect its chemical utilization. The higher boiling resins and greases are worthy of attention by future chemical investigators, as they are present in considerable quantity, and further amounts of the resins are left in the 460° F. melting point pitch, although this (containing from 50 to 60 per cent of free carbon and considerably harder than ordinary commercial pitches) is very close to pitch coke. The method of tar distillation was such as to minimize cracking, as shown by the fact that the 460° F. pitch was entirely fluid when drawn from the still.

The writers believe that the results given are new and afford a better picture of the constituents of American coke-oven tar than has heretofore been available. They may serve to correct many misconceptions which have been prevalent in the past, and should indicate certain fields in which effort toward the isolation and utilization of coal-tar products is desirable.

A New Ethylating Agent

For some time the Mellon Institute of Industrial Research, University of Pittsburgh, Pittsburgh, Pa., in connection with the work of the Multiple Industrial Fellowship sustained by the Carbide & Carbon Chemicals Corp., of New York City, has been making a thorough investigation of the properties and uses of diethyl sulfate as a general ethylating agent. A. R. Cade, an industrial fellow of the institute, under whom the greater part of this work has been carried out, has published recently a report of the findings of this investigation, which report shows diethyl sulfate to be a most satisfactory general reagent for introducing ethyl groups into organic compounds.

Mellon Institute will be pleased to furnish samples of this material to those interested, and Mr. Cade will correspond gladly with any one who desires further information upon this subject. Reprints of the article referred to may be obtained by writing to Mr. Cade at the institute.

U. S. Patent 1,355,103 (October 5, 1920).

The Surface Tension Balance[1]

Apparatus for the Rapid Measurement of Surface Tension

By Robert Gladding Green

University of Minnesota, Minneapolis, Minn.

A new type of surface tension balance is described, an apparatus utilizing the drop weight method of measuring surface tension of liquids. Less than five drops of liquid are necessary for measurement. No calculations are used and the drop weights are not actually determined. The surface tension is indicated upon the scale directly in dynes per centimeter.

With the increasing application of physical and colloidal chemistry to biological science and the industries, surface phenomena are being recognized as of great importance and the measurement of surface tension is accordingly becoming a very common procedure. Experimental work involving large numbers of surface tension determinations has been carried on in these laboratories for a number of years, and a special study has been made to develop apparatus and methods suitable for biochemical investigation. While rapidity of measurement has been considered of prime importance, it has been required that the procedures give standard values of reasonable accuracy. For results of different investigations and of various investigators to be comparative, it is essential that data be reported in true standard units. All methods of surface tension measurement require correction to give standard values, but as the correction in case of the drop weight method can be made so small as to be negligible, this method has been adopted for general use. For use with the drop weight method two types of torsion wire balances have been developed. Such an apparatus has been termed a surface tension balance.

A torsion wire balance was used by Searle[2] for the measurement of surface tension, the degree of torsion being determined by the use of weights. DuNuoy[3] introduced the production of torsion in one end of the torsion wire, and also its indication by means of a scale divided into degrees. In a preliminary description of this apparatus[4] an adjustable scale has been introduced, which has made it possible to express the torsion of the wire in standard units of surface tension so that readings are made directly in dynes per centimeter.

Description

The two types of our surface tension balance are designated as Type A and Type B. The apparatus built as used in these laboratories is easily convertible from one type to the other. In general, the apparatus consists of three mechanical parts, a dropping pipet, a balance beam mounted upon a torsion wire, and an adjustable scale. The dropping pipet is similar to those used for actual drop weights. The balance beam (*CB*, Fig. 2) supported by the torsion wire *D* carries at one end a silver cup, *C*, pivoted upon watch jewels. The adjustable scale consists of a series of arcs of the same radius, but the segments are of different lengths and each segment is divided into the same number of units by lines normal to the arcs. This division into units is different in Type A and Type B. The scale face is movable horizontally so that any one of the series of arcs can be moved under the end of the pointer. The scale is so constructed in relation to the size of the torsion wire that the units represent surface tension in dynes per centimeter.

Type A balance is similar in design to the apparatus described in the preliminary paper.[4] Here the balance beam swings to an angular position when a drop of the liquid to be measured is dropped into the cup. The adjustable scale is so placed that the end of the beam opposite the cup acts as a pointer and swings over the scale face indicating the surface tension in dynes per centimeter. At the angular position of equilibrium the force acting upon the balance beam may be expressed by the equation $\Theta c = w\gamma \cos\Theta$, where Θ = angle of torsion of the wire, c = torsion constant of the wire, w = weight of liquid drop used, and r = length of balance beam from torsion wire to cup. This may be written $w = k\frac{\Theta}{\cos\Theta}$, as c and r are constants. We also have Tate's law, $\gamma = kw$, where γ = surface tension and k = constant. Combining the two equations, we have $\gamma = k\frac{\Theta}{\cos\Theta}$.

This relation indicates that a scale reading surface tension directly in dynes per centimeter when used on this type of balance must be so constructed that the size of the units will decrease as the angle of torsion increases. As the relation between Θ and $\cos\Theta$ is purely geometrical, such a scale can be accurately constructed, and is pictured in Fig. 1.

Type A surface tension balance is the simplest and most rapid to operate. It has a limitation of accuracy as the function $\Theta/\cos\Theta$ decreases rapidly with large values of Θ.

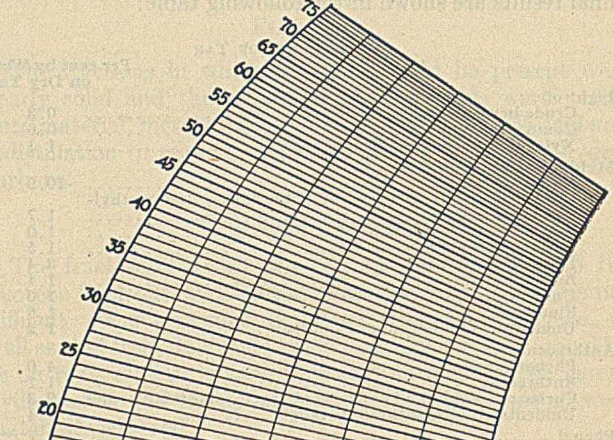


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Fig. 1—Scale on Type A Balance

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[1] Received April 28, 1923.

[2] *Proc. Cambridge Phil. Soc.*, **17**, 285 (1914).

[3] *J. Gen. Physiol.*, **1**, 521 (1919).

[4] *J. Bact.*, **7**, 367 (1922).

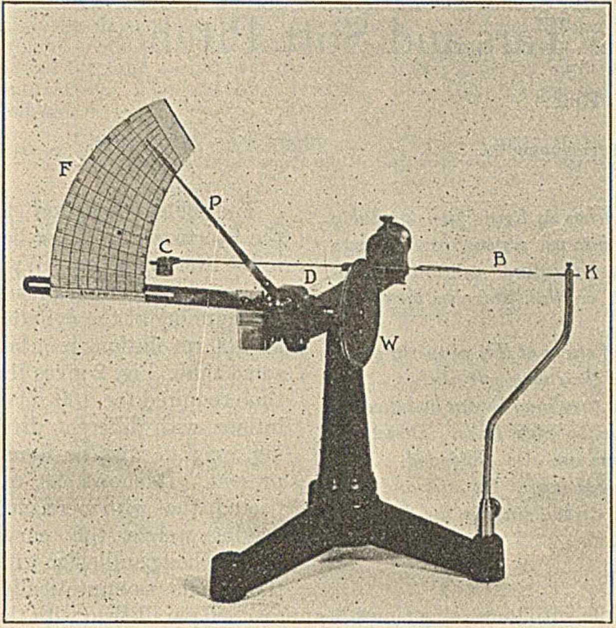

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FIG. 2—TYPE B SURFACE TENSION BLOWER

This type of apparatus is calibrated by the use of a standard solution, preferably with a low surface tension, as benzene, and finds its application where rapidity and ease of manipulation is desired.

Type B apparatus is pictured in Fig. 2. In this type the balance beam at equilibrium is in the horizontal position, the zero point being determined by the indicator *K*. Angular displacement of the balance beam due to the weight of the liquid dropped into the cup is counterbalanced with torsion produced by rotation of one end of the wire. As torsion is produced in the wire by means of the wheel *W*, the pointer *P* moves over the scale face and indicates the surface tension of the liquid in dynes per centimeter when the balance beam is again in the horizontal position. At equilibrium the balanced forces are expressible in the notation used above as $\Theta c = wr$, and combining this with the law of Tate, $\gamma = k\Theta$, indicating that in this type of apparatus the units representing surface tension are proportional to the angles of torsion. Such a scale is shown constructed in Fig. 3.

CALIBRATION

The pointer is set at zero dynes and the balance beam brought opposite the horizontal indicator. Two or three drops of pure water (or other standard liquid of known surface tension) are dropped from the dropping pipet into the cup. The beam is balanced in the horizontal position by torsion in the end of the wire, the pointer moving to some angular position upon the scale face. In the case of water at 25° C., this angular displacement represents 72.8 dynes. On the scale face among the series of arcs there will be found one which will correspond to this angular displacement and will be divided into 72.8 units. The scale face is moved laterally until the reading off the end of the pointer is 72.8 and the apparatus is calibrated. This process is carried out quickly and conveniently each time the balance is used or the pipet cleaned, and it is also desirable to check the calibration after running a series of measurements. The pipet is the only part of the apparatus to be cleaned, as the cup need only be dried and the balance beam checked for zero reading. With pure water and careful manipulation repeated calibrations of the instrument will check within one or two tenths of a dyne.

The number of drops used depends upon the size of the torsion wire; two or three drops have been found very convenient. The adjustability of the scale allows for a variation of 30-degree angular displacement of the pointer, and this coupled with the choice of size of torsion wire used and the number of drops employed gives the apparatus great flexibility.

Evaporation and temperature are the gross sources of error. With water and watery solutions the evaporation error is minimized in that calibration and measurements are made under similar conditions of evaporation. The temperature error may be made small by control of room temperature or by frequent calibration.

It is essential that the water used in calibration of the apparatus be very pure, as minute traces of some substance markedly reduce surface tension. It has been practice to use freshly redistilled water for calibration of this instrument, accepting the surface tension of this liquid as 72.8 dynes at 20° C.

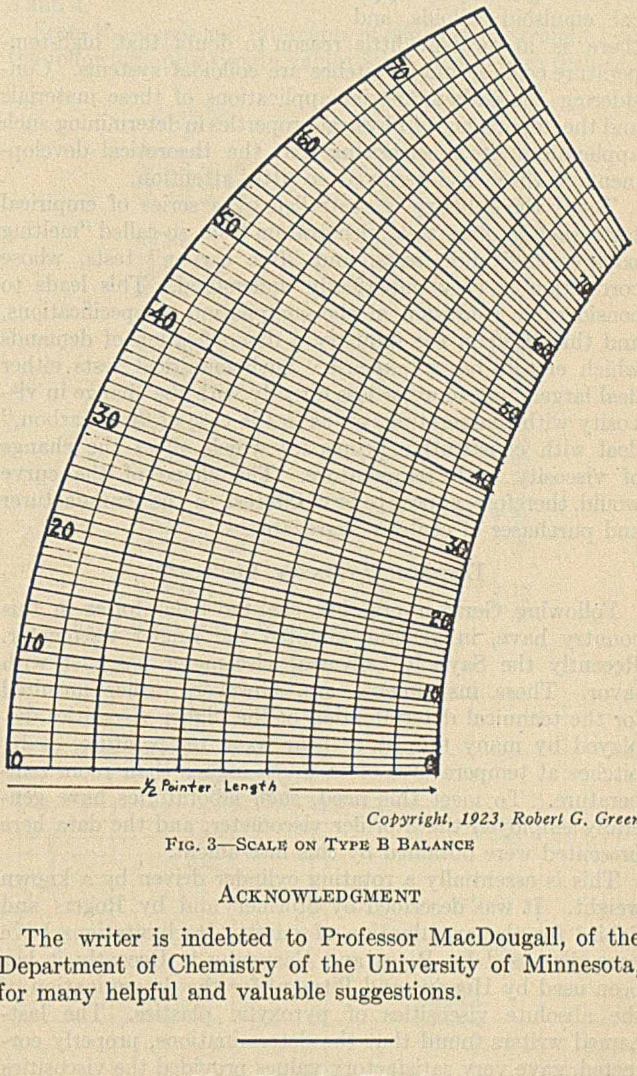

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FIG. 3—SCALE ON TYPE B BALANCE

ACKNOWLEDGMENT

The writer is indebted to Professor MacDougall, of the Department of Chemistry of the University of Minnesota, for many helpful and valuable suggestions.

New Uses for Wood

Chemical research is revealing new uses for wood that were not dreamed of a few years ago, declares the Forest Service, Department of Agriculture. One example is that of the extended use of pulpwood, not only for paper products, but also for fiber containers, wall board, and similar forms of material. Wood is already in use for the making of artificial silk, rope, carpets, and other fabrics.

The Viscosity of Coke-Oven Tars and Soft Pitches[1]

By Wilbert J. Huff

The Koppers Company, Pittsburgh, Pa.

In the utilization of tar and soft pitches as liquid fuel, probably no property influences the design of pumps, piping, and burners more than the change of viscosity with temperature; yet, to the chemist and engineer seeking information on this property very little is available in the literature.

This paper gives the results of a brief study of this property using a number of typical coke-oven tars and their very soft pitches. The results are expressed in such units that they may be applied directly to the calculation of the pressure drop in pipe lines. Directions and formulas covering such calculations are also appended.

The viscosity data should also prove useful for still and condenser design in connection with the carbonizing or tar-distilling plant.

THE general shape of the viscosity-temperature curves for the tars and pitches when plotted on ordinary coördinates is illustrated by Fig. 1. The sharp bend is characteristic. The smooth yet rapid transition of the coal-tar pitch aggregate from a liquid so viscous that it is brittle to a mobile fluid resembles in general the corresponding change in typical emulsoid colloids, and there is at present little reason to doubt that high-temperature coal tar and its pitches are colloidal systems. Considering the wide industrial applications of these materials and the importance of physical properties in determining such applications, it is surprising that the theoretical development of these has received so little attention.

Today the industry is controlled by a series of empirical tests, such as float tests, penetration tests, so-called "melting point tests," slide tests, and "free carbon" tests, whose correlation is very imperfectly understood. This leads to considerable confusion in the compilation of specifications, and throws upon the industry a diversification of demands which entails heavy expense. Such empirical tests either deal largely and more or less directly with the change in visvosity with temperature, or, as in the case of "free carbon," deal with constitutive properties which affect the change of viscosity with temperature. The shape of the curve would, therefore, appear to be of interest to the manufacturer and purchaser of coal-tar aggregates.

Determination of Viscosity

Following German practice, coal-tar laboratories in this country have, in general, adopted the Engler viscometer. Recently the Saybolt Universal viscometer has met with favor. These instruments are, however, rather unsuited for the technical determination of the higher viscosities displayed by many tars at or near room temperature, or by pitches at temperatures often much higher than room temperature. To meet this need, such laboratories have generally employed the Stormer viscometer, and the data here presented were obtained by this instrument.

This is essentially a rotating cylinder driven by a known weight. It was described by Stormer[2] and by Rogers and Sabin[3] for the examination of paint. Its limitations have been discussed by Riggs and Carpenter.[4] Recently it has been used by Higgins and Pitman[5] for the determination of the absolute viscosities of pyroxylin plastics. The last-named writers found that the determinations, properly corrected, gave very satisfactory values provided the viscosities were greater than 15 centipoises.

The chief objection to the Stormer viscometer lies in the friction factor. With no liquid in the instrument, the spinning of the cylinder for 100 revolutions requires some time. Fig. 2 gives the time required for 100 revolutions with different driving weights with no liquid present. It shows, as expected, that with increasing driving weight the curve approached parallelism with the x-axis asymptotically, while with increasing times it approached parallelism with the y-axis asymptotically, and suggests a hyperbola. Determinations of points on the curve with driving weights less than 10 grams proved difficult, because slight variations in the character of the initial impulse seriously affect the time required for 100 revolutions.

Since the curve approaches parallelism with the respective axes with high driving weights and high times, the instrument appears capable of giving comparative viscosities under these conditions, especially when the driving weight remains constant throughout, a precaution observed in the experiments reported herewith.

Thus, Higgins and Pitman found that sufficiently high viscosities with high driving weights gave values which could be expressed by the straight-line equation $V = At - B$, where B is the correction factor.

An attempt to determine, for the instrument employed, the constants of the Higgins and Pitman equation, using as calibrating liquids two glycerol solutions having densities lying in the region from 1.20 to 1.23, however, gave a slight positive value for B. This may have been due to some unknown experimental error, or to the doubt which lies upon the true viscosities for solutions of glycerol in this region.[6]

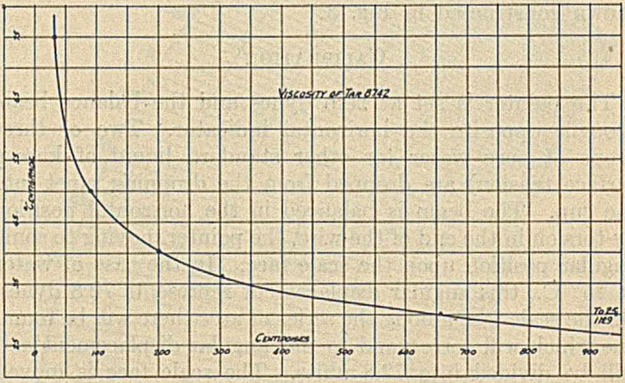

Fig. 1

The readings were, therefore, converted to absolute viscosities as follows:

The time for a carefully calibrated petroleum oil having a viscosity of 29.9 centipoises was found to be 13.5 seconds with a driving weight of 126.9 grams. The weight necessary to over-

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[1] Presented before the Section of Gas and Fuel Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] *Oil, Paint Drug Rep.*, **27** (1911), through *Petroleum* **6**, 2184 (1920).

[3] This Journal, **3**, 737 (1911).

[4] *Ibid.*, **4**, 901 (1912).

[5] *Ibid.*, **12**, 587 (1920).

[6] Herschel, *Bur. Standards, Tech. Paper* **112**, 23.

come the friction of the empty viscometer at a time of 13.5 seconds was determined from Fig. 2 and subtracted from the driving weight. For each observation a similar correction was made. When the time was greater than 25 seconds a constant value was subtracted. The absolute viscosity was then calculated as follows:

$$29.9 \times \frac{\text{Observed time for tar or pitch}}{\text{Observed time for petroleum oil}} \times \frac{\text{Corrected weight for tar}}{\text{Corrected weight for petroleum oil}}$$

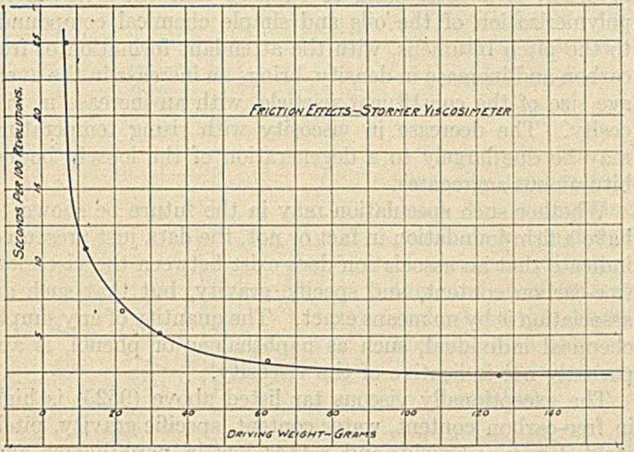

Fig. 2

This procedure is not entirely satisfactory and involves certain assumptions not strictly true. It does, however, give absolute viscosities sufficiently accurate for engineering purposes. Moreover, most of the viscosities of the tars and pitches measured are so high that they are undoubtedly comparative *inter se*. The general form of the interpolation equation to be discussed later is, therefore, not seriously affected by the friction correction.

Much of the criticism of Riggs and Carpenter against the Stormer viscometer may be dismissed, because it was based upon determinations made in the region where the friction correction curve undergoes a sharp bend. The instrument does, however, possess a number of faulty features. Thus, the bath is too small, making the maintenance of constant temperature difficult, and the mechanical suspensions faulty, so that it is necessary for the operator to be constantly on guard against improper alignments.

There is a great need for a satisfactory viscometer of this type. The absence of easily procured calibrating liquids of high viscosity has hitherto hindered the introduction of the McMichael viscometer.

Scope of the Data

A survey of present practice at a number of plants using tar as a fuel showed that these installations in general had little or no difficulty in handling this material where its viscosity was less than approximately 100 centipoises, but that pumping troubles were generally encountered when the viscosity rose above this figure. This study was, therefore, directed towards the shape of the viscosity-temperature curve in this region.

The pitches examined were representative distillation residues whose viscosity in general could be reduced to approximately 100 centipoises or less within the range of steam heating.

Viscosity-Temperature Curve

Figs. 3 and 4 illustrate typical data so obtained. The viscosity-temperature relationships can best be shown graphically on log-log coördinates in which the temperature in degrees centigrade is plotted against the viscosity in centipoises, since the resulting graph is a flat curve which for all practical purposes may be regarded as a straight line. Thus, for interpolation purposes, the viscosity-temperature equation may be expressed as

$$\log z = \log K - n \log T_c \text{ or } z = \frac{K}{T_c^n}$$

where z is the viscosity, K is a constant, n is a constant, and T_c is the temperature in degrees centigrade.

A similar equation is given by Bateman[7] for the change in the viscosity of high-boiling creosote and carbolineum oils with change in temperature. It is perhaps of interest to point out that these interpolation equations form only a special case of the rather general empirical equation employed by Thorpe and Rodgers in their classical work on viscosity—viz.,

$$z = \frac{a}{(b + T_c)^n}$$

This was first proposed by Slotte.[8,9]

In order to indicate possible variations in the character of the viscosity-temperature curves for a number of different tars and their soft pitches, the writer has plotted such data. In every case the points on log-log coördinates obeyed approximately the straight-line relationship shown on Figs. 3 and 4.

From the slopes and intercepts of the various straight lines the following approximate values for K and n were deduced:

Condition	Logarithm of— K^a	Logarithm of— n
	Tar 8742	
Raw tar	8.23	3.66
20.2% oil off	16.10	7.03
22.7% oil off	16.25	7.00
26.2% oil off	16.90	7.22
	Tar 9522	
Raw tar	8.04	3.56
15% oil off	13.52	5.80
18% oil off	13.82	5.85
20% oil off	14.90	6.30
	Tar 9523	
Raw tar	8.05	3.52
19% oil off	14.50	6.20
22.3% oil off	16.00	6.85
26.2% oil off	18.30	7.25
	Tar 9524	
Raw tar	6.10	2.58
21.2% oil off	12.90	5.65
22.6% oil off	13.15	5.65
27% oil off	14.40	6.20
	Tar 9525	
Raw tar	10.52	4.44
7.2% oil off	15.50	6.59
14.2% oil off	17.20	7.06
	Tar 10859	
Raw tar	6.98	3.13
22.6% oil off	12.30	5.26

[a] All logarithms given have 10 as the base.

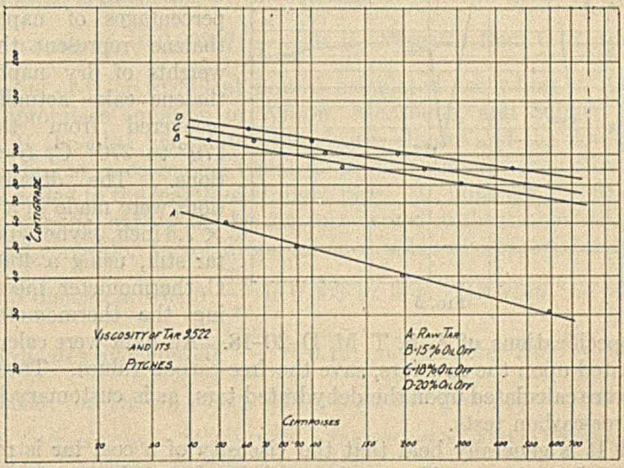

Fig. 3

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[7] *U. S. Dept. Agr., Bull.* **1036**, 54.

[8] Bingham, "Fluidity and Plasticity," **1922**, p. 130. McGraw-Hill Book Company, New York City.

[9] A more exact approximation curve would probably be obtained if this general equation were used. It is, however, cumbersome.

It should of course be remembered that these constants apply only to temperature and viscosity conditions within or near the limits adopted for this study.

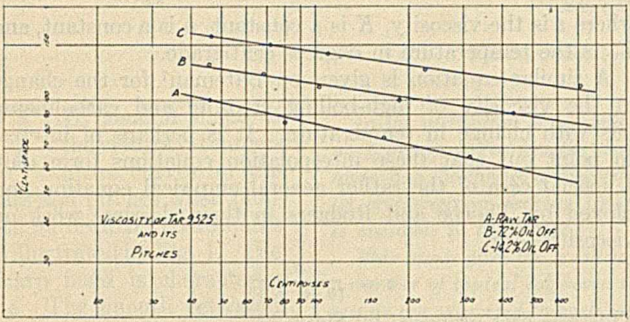

Fig. 4

Viscosity of Tar and Other Properties

The variation in viscosity from tar to tar suggests the interesting possibility of some correlation between this property and other properties. Unfortunately, data upon these tars were accumulated to meet certain technical exigencies, and, at the time, the compilation into a viscosity–temperature study was not contemplated, so certain relationships which might be of interest could not be developed. Following is some of the information available:

Tar No.	Specific Gravity at 15.5°/4° C.	Water %	Free Carbon %	Crude Tar Acids %	Naphthalene Cake %	Anthracene Cake %
8742	1.183	1.5	4.86	2.6	3.2	1.6
9522	1.149	2.3	(*a*)	1.5	2.5	1.5
9523	1.165	1.5	7.07	1.7	4.3	...
9524	1.163	1.0	6.35	0.3	10.5	...
9525	1.237	3.0	(*b*)	0.7	3.5	1.2
10859	1.166	2.0	....	1.4	5.8	1.9

[a] Another sample gave 4.28 per cent free carbon.
[b] Another sample gave 11 per cent free carbon.

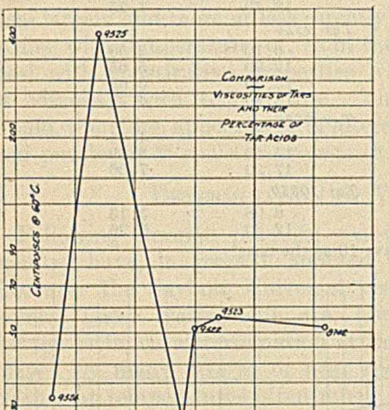

Fig. 5

The relative oil–pitch yields may be judged by reference to the table of constants just preceding.

The percentages of tar acids given are the percentages of crude acid actually recovered from the 170° to 235° C. fraction, while the percentages of naphthalene represent the weights of dry naphthalene cake actually recovered from the 170° to 270° C. fractions. The distillations were made in a 5 × 7.5 inch, Jayne type, tar still, using a 400° C. thermometer, meeting the thermometer specifications of A. S. T. M. D–20–18. All data were calculated upon the raw tars, save the free-carbon values. These were calculated upon the dehydrated tars, as is customary in free-carbon tests.

It is generally held that the viscosity of a coal tar is related to its specific gravity and its free-carbon content. Unfortunately, data upon the free-carbon content of these tars were not complete. For another series of tars, however, viscosity,[10] specific gravity, and free-carbon data were available and these are shown graphically in Figs. 7 and 8. A graphic comparison between the viscosities of the tars listed above and their percentages of crude tar acids and crude naphthalene cake is shown in Figs. 5 and 6.

The data are insufficient to formulate a complete explanation of the viscosity of coke-oven tars and their pitches and the change of viscosity with temperature. If speculation is in order, it is interesting to suppose that the pyrogenetic polymerization of the oils and simple chemical compounds to the pitch bitumens, with the attendant formation of free carbon and increase in density, brings an increase in the average size of the constituent particle, with an increase in viscosity. The decrease in viscosity with rising temperature may be due largely to a degeneration of the loosely bound bituminous aggregates.

Whether such speculation may in the future be shown to have a firm foundation in fact or not, the data just presented indicate that an association does exist between the viscosity, free-carbon content, and specific gravity, but that such an association is by no means exact. The quantity of any simple chemical individual, such as naphthalene or phenol, is apparently not indicative of the viscosity.

The exceptionally viscous tar listed above (9525) is high in free-carbon content, water content, specific gravity, pitch yield, low in oil yield, and rather low in naphthalene and tar acids.

Change of Viscosity of Tars and Pitches with Changing Oil Content

The experimental values detailed here do not show accurate correlation between the volume of the oil distilled from the tar and its increase in viscosity with such distillation. This is no doubt partly due to the fact that distillation losses of varying magnitudes occurred in the preparation of the pitches, but many other factors enter. Thus, it is well known that the oils themselves undergo an increase in viscosity with continued heating, ultimately giving the pitch resins or the free carbon, and that this increase depends upon thermal conditions and other variables. The character of the pitch obtained at a given oil yield may therefore vary with distillation conditions. A minor error is the partial crystallization of the distillates.[11] Our present information is too limited to permit a correlation to be calculated from any theoretical considerations.

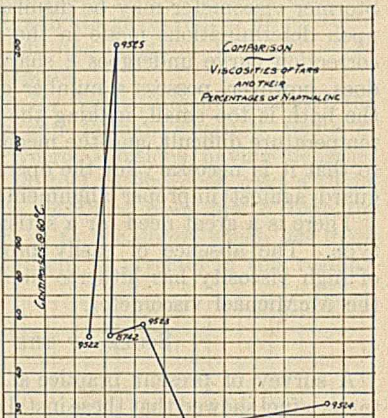

Fig. 6

The tar distiller and the project engineer, however, will find it necessary to estimate this change in some manner. Given the viscosities of the tar and one pitch, a simple method of approximating the viscosity of a pitch not greatly different is to assume that the change in temperature for viscosities of approximately 100 centipoises is linear with the amount of oil distilled from the tar. The new curve is then drawn on log-log coördinates parallel to the pitch curve already known.

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[10] The viscosities shown in Figs. 7 and 8 were determined by means of the Saybolt Universal viscometer.

[11] Huff, This Journal, 10, 1017 (1918).

In cut-back operations, where the oil is added to the pitch and the viscosity of each is known, the viscosity of the mixture may be calculated from an equation given by Bateman[12]—viz., $V_m = (V_t^p)(V_c^{1-p})$ where V_m is the viscosity of the solution, V_t the viscosity of the tar, and V_c the viscosity of the oil, and p is the percentage of tar used expressed as a decimal.

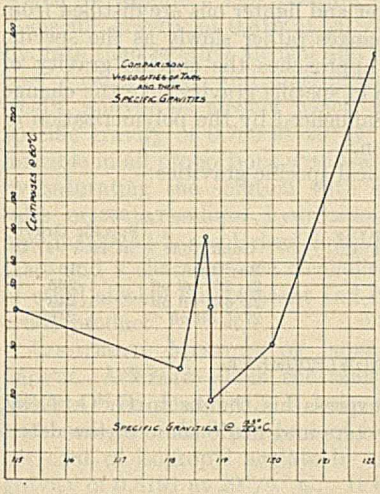

Fig. 7

Application of the Viscosity–Temperature Data in Design

The application of viscosity–temperature data to engineering problems in the design of piping is so important and so often misunderstood that a brief abstract of a satisfactory procedure appears to be justified.

The movement of liquids in tubes may occur in either of two conditions, viscous (straight line flow) or turbulent flow. The first is expressed by the law of Poiseuille:

$$P = \frac{0.000668\,zlv}{D^2}$$

and the second by the modified Fanning equation:

$$P = \frac{0.323\,flsv^2}{D}$$

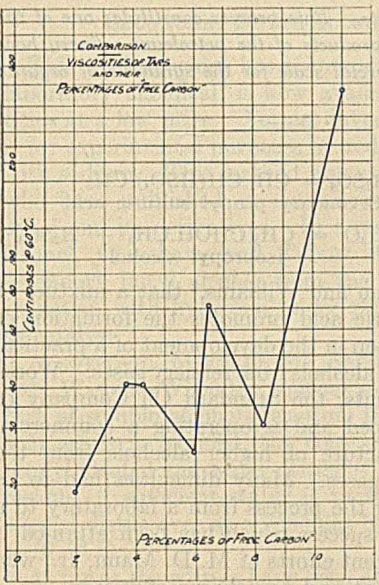

Fig. 8

where P = pressure drop (pounds per square inch)
z = viscosity of the liquid (in centipoises)
s = specific gravity of the liquid (referred to water at 4° C.)
l = length of pipe (feet)
D = inside diameter of the pipe (inches)
v = average linear velocity in pipe line (feet per second)
f = Fanning friction factor

Between these two conditions there exists a critical region which for commercial pipe lines is fixed by the relationship $\frac{Dvs}{z}$ = approximately 0.12. In this region the flow is irregular and may take on the characteristics of either region. Blausius has pointed out that the equations take the same form if $f = 0.00207\,\frac{z}{Dvs}$. This applies to viscous flow.

A number of experimenters have developed relations between $\frac{Dvs}{z}$ and turbulent flow effects. At the suggestion of W. K. Lewis, this correlation has recently been investigated in detail and applied to commercial installations by a group of workers at the Massachusetts Institute of Technology. The results of this work were published by Wilson, McAdams, and Seltzer.[13] These show that the turbulent flow curve for commercial pipe lines may be approximated by the equation:

$$f = 0.01\left(\frac{z}{Dvs}\right)^{0.2}$$

or more exactly by the equation

$$f = 0.0035 + 0.00594\left(\frac{z}{Dvs}\right)^{0.424}$$[14]

A graph for this equation is given in the paper cited.

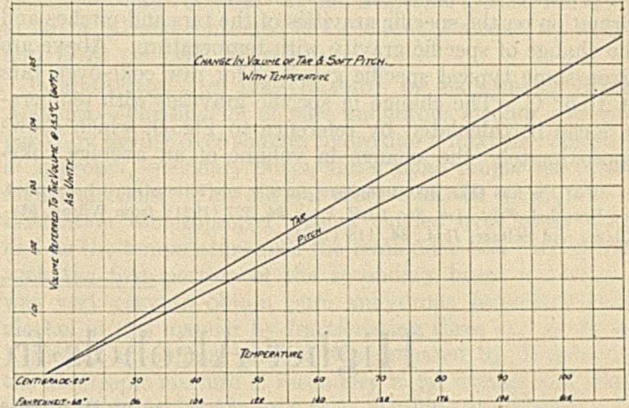

Fig. 9

With this information it is possible to calculate readily the pressure drop in pipe lines conveying tars or pitches in either viscous or turbulent flow.[15]

The first step involves the calculation of $\frac{Dvs}{z}$. If this is less than 0.12, showing viscous flow, the Fanning friction coefficient is calculated by the equation of Blausius given above—namely, $f = 0.00207\,\frac{z}{Dvs}$. If it is greater than 0.12, the value of f for turbulent flow is calculated according to the appropriate equation of Wilson, McAdams, and Seltzer.

If the pipe line contains 90-degree elbows and the flow is turbulent, a correction equal to 30 diameters for each elbow is added to the length of straight pipe. If, however, the flow is viscous, data given by the last-named authors show that this correction factor drops off to a value of approximately 2.5 diameters where $\frac{Dvs}{z}$ is 0.003 or less. Between the coordinates diameter 30, $\frac{Dvs}{z} = 0.12$; and diameter 2.5, $\frac{Dvs}{z} = 0.003$; on log-log paper, this correction curve approximates

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[12] *U. S. Dept. Agr., Bull.* **1036**, 83.

[13] This Journal, **14**, 105 (1922). The writer is indebted to this article for the information contained in this section.

[14] A very similar equation had previously been proposed by Lees for turbulent flow in smooth pipes.

[15] At the higher viscosities, tar and pitch may take on the properties of a plastic solid. It therefore appears advisable to so design the piping equipment that viscosities of 100 centipoises or less may be always secured. Cf. A. Pochettino, *Nuovo cimento*, **8**, 77 (1914), from *C. A.*, **11**, 2980 (1917).

a straight line. For values of $\frac{Dvs}{z}$ below 0.003, 2.5 D may be taken as the correction.[16]

Knowing f and the corrected value for l, it is then only necessary to substitute these values in the Fanning equation:

$$P = \frac{0.323\, flsv^2}{D}$$

This is done irrespective of whether the flow is viscous or turbulent.

Coal tar and its pitches show a tendency to deposit solid matter on horizontal surfaces, thus restricting the effective diameter. Accordingly, a large factor of safety should be allowed in the application of these calculations.

SPECIFIC GRAVITIES OF TARS AND PITCHES

To apply this procedure it is necessary to have some information on the specific gravities of the tars and pitches and the change of specific gravity with temperature. Above are given some typical specific gravities for raw coke-oven tars at 15.5° C. The change in specific gravities with temperature can be calculated by reference to Fig. 9, which shows approximately the change in volume of an average coke-oven tar and of an average soft pitch with change in temperature. Values so represented are only approximate, because the coefficient of expansion varies with the tar and pitch and also with the temperature, but present information does not justify refinements beyond simple linear relations as shown, and these are probably sufficiently accurate for all ordinary engineering data.

The specific gravity of the pitch residue at 15.5° C. rises rapidly at first as the water and lighter oils are distilled from the tar; after that it changes rather slowly as the specific gravity of the distillate approaches the specific gravity of the residue. The change in specific gravity, like the change in viscosity, is probably influenced by the polymerization of the oils during distillation.

Following are some typical specific gravities:

Tar 9522		Tar 9524	
Condition	Specific Gravity at 15.5°/4° C.	Condition	Specific Gravity at 15.5°/4° C.
Raw tar	1.149	Raw tar	1.16
15% oil off	1.214	21.2% oil off	1.233
18% oil off	1.215	22.6% oil off	1.243
20% oil off	1.222	27% oil off	1.246

ACKNOWLEDGMENT

The writer wishes to express his thanks to G. G. Désy, who distilled some of the tars and made some of the determinations included here.

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[16] If l is less than 300 diameters, further corrections must be applied. See Herschel, *Proc. Am. Soc. Civil. Eng.*, **84**, 527 (1921), from Wilson, McAdams and Seltzer, *Ibid.*, **84**, 118 (1921).

Higher Alcohols from Petroleum Olefins[1]

By W. W. Clough and Carl O. Johns

STANDARD OIL COMPANY OF NEW JERSEY, ELIZABETH, N. J.

This paper presents the chemical properties and physical constants of some secondary higher alcohols manufactured from the olefins formed in the commercial cracking of petroleum oils. New azeotropic mixtures of some of these alcohols with water and with the alcohols and their acetates are described. The alcohols obtained by this process thus far have all been normal secondary alcohols. The availability of this series of alcohols, all of which have hitherto been very rare, should furnish the organic chemist with raw materials for the synthesis of a wide range of organic compounds. A few derivatives of the alcohols are described and some of these will add to our list of organic solvents. This process constitutes one of the few cases in which the by-products of the petroleum refinery have been employed on a commercial scale for the synthesis of organic compounds.

CRUDE petroleum is practically devoid of olefins, but these compounds are formed in large quantities in the pyrolytic decomposition of mineral oils at elevated temperatures. Since pyrolysis is carried out on an extensive scale in the cracking of the heavier oils to produce gasoline, a very large supply of olefins is available from this source.

The chemistry of cracking of oils is not fully known, since the decomposition may proceed in various ways according to the conditions employed and the chemical constitution of the molecules which are cracked. There is evidence, however, that in its simplest form cracking consists in the splitting of the large molecules into saturated and unsaturated hydrocarbons. Thus, decane might decompose into pentane and amylene as follows:

$$\underset{\text{Decane}}{CH_3.(CH_2)_8.CH_3} = \underset{\text{Pentane}}{CH_3.(CH_2)_3.CH_3} + \underset{\text{Amylene}}{CH_3.(CH_2)_2.CH = CH_2}$$

Olefins combine with sulfuric acid to form alkyl acid esters and when such acid esters are hydrolyzed they produce alcohols and sulfuric acid. These reactions may be shown as follows:

$$\underset{\text{Propylene}}{CH_3.CH = CH_2} + H_2SO_4 = \underset{\text{Secondary propyl sulfuric acid}}{CH_3.CH(HSO_4).CH_3}$$

$$CH_3.CH(HSO_4).CH_3 + H_2O = \underset{\text{Isopropyl alcohol}}{CH_3.CHOH.CH_3} + H_2SO_4$$

The discovery by Mann and Williams,[2] that a mixture of a mineral oil and sulfuric acid promotes the formation of esters, is an important step in the development of a practical process of manufacturing alcohols from refinery gases. Working under assigned patents, the Standard Oil Company of New Jersey has developed and is operating a commercial process for the manufacture of higher alcohols from the olefins in pressure still gases. Many difficulties had to be overcome in transferring the process from a laboratory to a commercial scale. The success which has been attained is chiefly due to the persistent efforts of M. D. Mann, Jr., who designed the alcohol plant and has charge of it.

The gases which are used for the manufacture of the alcohols contain a mixture of olefins from which isopropyl and secondary butyl, amyl, hexyl, heptyl, and octyl alcohols are obtained. These are produced in decreasing proportions in the order just stated. All of these alcohols made thus far in a pure state have been normal secondary alcohols—that is, alcohols containing the hydroxy group on the second car-

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[1] Presented before the Division of Petroleum Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] U. S. Patent 1,365,043 (1921).

bon atom of a straight-chain hydrocarbon. Although ethylene is present in the gases, there is no evidence of the formation of ethyl alcohol as the process is now operated.

Isopropyl Alcohol, 2-Propanol

The rectified alcohol[3] is obtained as a constant boiling mixture containing 91 per cent of alcohol and 9 per cent of water by volume. This mixture boils at 80.4° C. and has a specific gravity of 0.816 at 20°/4° C. It is easier to dehydrate than is ethyl alcohol and a short digestion with excess of caustic soda and subsequent distillation gives a practically anhydrous alcohol which boils at 82.4° C., with a specific gravity of 0.785 at 20°/4° C. Isopropyl alcohol is miscible in all proportions with water, but may be salted out by saturating the solution with sodium chloride or other salts or with sodium hydroxide. The isopropyl alcohol now marketed is a colorless liquid having a somewhat bitter taste and a characteristic alcoholic odor different from that of ethyl alcohol but pleasant and free from the odors of the crude product.

Azeotropic Mixture of Isopropyl Alcohol and Isopropyl Acetate—This constant boiling mixture has not hitherto been described. It boils at 80.1° C. and 760 mm., and consists of 52.3 per cent of isopropyl alcohol and 47.7 per cent of isopropyl acetate by weight. It has a specific gravity of 0.8191 at 20°/4° C. It has a pleasant odor and is an excellent solvent for many organic compounds.

Isopropyl Chloride[4]—This compound is easily made by slowly distilling a mixture of isopropyl alcohol and concentrated aqueous hydrochloric acid. To insure the best results it is necessary to employ a column of sufficient fractionating capacity to permit the chloride to distil over with as little alcohol as possible. This is relatively easy since the chloride boils at 36.5° C. and the alcohol at 80.4° C. Isopropyl chloride is an excellent solvent for fats, and while it may be ignited it burns slowly and the flame is easily extinguished.

Secondary Butyl Alcohol, 2-Butanol

This alcohol, which has been known hitherto only as a rare laboratory chemical, is now available in commercial quantities at a low price. Former investigators usually prepared it for experimental purposes by reducing methylethyl ketone with sodium. This method was used by Norris and Green,[5] who have published an extensive investigation on this alcohol and its derivatives. In a recent very excellent paper, Brunel, Crenshaw, and Tobin[6] state that they prepared secondary butyl alcohol from the corresponding ketone by reduction with hydrogen under pressure, using nickel oxide as catalyst.

Azeotropic Mixture of Secondary Butyl Alcohol and Water—When the aqueous solution containing the mixture of soluble alcohols resulting from the hydrolysis of the acid esters is rectified, the constant boiling mixture of isopropyl alcohol and water distils over at 80.4° C. From this residue, if sufficient water is present, the secondary butyl alcohol distils over as a constant boiling mixture with water at 87.5° C.

As far as the writers have been able to ascertain, this azeotropic mixture is not described in the literature. It was discovered by Mann and Lebo in the alcohol plant of this company while fractionating an aqueous solution which contained chiefly secondary butyl alcohol admixed with a small proportion of other alcohols. The initial fractionation was made on a charge of 1000 gallons with a 30-plate, 20-foot fractionating column. A portion of this distillate was later re-run in a glass laboratory still, which has also been used for the final fractionation of the other distillates described in this paper. This still was designed by Buc and consists of a glass column 2 meters high and of 5 cm. internal diameter. The column is filled with glass tubes with an internal diameter of about 5 mm. and 25 mm. long. These tubes are constricted somewhat at both ends and are placed in the column so that the liquid will readily drain out of them. This fractionating column can readily be adapted to stills of different sizes.

A portion of the secondary butyl alcohol which had previously been fractionated in the large still was re-run in the glass still and was found to boil at a constant temperature of 87.5° C. and 760 mm. It had a specific gravity of 0.8620 at 20°/4° C. and contained 72.7 per cent of alcohol by weight and 77.72 per cent by volume.

Purification and Dehydration of Secondary Butyl Alcohol—The first lot of pure anhydrous alcohol was prepared by drying over sodium hydroxide a mixture consisting of isopropyl, secondary butyl, and a small proportion of still higher alcohols. This did not remove all the water, but on distillation the isopropyl alcohol carried over some water and as the temperature rose the remainder was carried over with the first portion of the secondary butyl alcohol. It was very easy to obtain pure anhydrous secondary butyl alcohol in this manner by fractionating three or four times. A second lot of pure alcohol was prepared by dehydrating the azeotropic mixture of secondary butyl alcohol and water with sodium hydroxide and then distilling the alcohol over aluminium amalgam. This method gave pure anhydrous alcohol very readily.

Determination of the Boiling Point of the Alcohol—Since ample quantities of secondary butyl alcohol which had been purified by the foregoing methods were available, the boiling point determinations were made by means of the glass still previously described, using two accurate Anschutz thermometers. The boiling point of both lots of purified alcohol was 99.40° C. at 760 mm. Brunel, Crenshaw, and Tobin obtained 99.53° C. at 760 mm. The value for $\frac{dT}{dp}$ in degrees per millimeter pressure was 0.036, or the same as that found by these authors.

Determination of Specific Gravity—Determinations were made in a 50-cc., vacuum-jacketed specific gravity bottle. The following results were obtained:

D 15°/4° C.	*D* 20°/4° C.	*D* 25°/4° C.
0.8104	0.8063	0.8027

The density at 25° C. agrees with that obtained by Brunel, Crenshaw, and Tobin.

The following alcohol-water mixtures were made by weighing the alcohol and water in a glass-stoppered bottle, and the specific gravities were determined at 20°/4° C.:

Per cent Alcohol by Weight	*D* 20°/4° C.
100.00	0.8063
89.50	0.8281
79.60	0.8465
69.31	0.8682
64.17	0.8797
Immiscible	
17.85	0.9732
10.00	0.9842
0.00	0.9982

The results were plotted to a large scale on cross-section paper so that 0.01 per cent of the volume and 0.0002 of the specific gravity could be read. These points were connected

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[3] Grant and Johns, *Am. J. Pharm.*, **94**, 418 (1922); Lebo, *J. Am. Chem. Soc.*, **43**, 1005 (1921); Curme, *Chem. Met. Eng.*, **25**, 1049 (1921).

[4] Linneman, *Ann.*, **136**, 41 (1865); Grant and Johns, *Am. J. Pharm.*, **94**, 424 (1922); U. S. Patent 1,436,377 (1922).

[5] *Am. Chem. J.*, **26**, 301 (1901).

[6] *J. Am. Chem. Soc.*, **43**, 561 (1921).

by a smooth curve and from this the following table was constructed. The temperature correction table was constructed by taking the specific gravities of the alcohol-water mixtures at 15°/4°, 20°/4°, and 25°/4° C.

TABLE I—SPECIFIC GRAVITY OF SECONDARY BUTYL ALCOHOL-WATER MIXTURES AT 20°/4° C.

Per cent by Weight	Per cent by Volume	Specific Gravity	Per cent by Weight	Per cent by Volume	Specific Gravity
0	0	0.9982	73	77.99	0.8614
1	1.24	0.9968	74	78.87	0.8594
2	2.47	0.9954	75	79.75	0.8574
3	3.70	0.9940	76	80.63	0.8554
4	4.92	0.9926	77	81.50	0.8534
5	6.14	0.9912	78	82.36	0.8514
6	7.36	0.9898	79	83.22	0.8493
7	8.58	0.9884	80	84.07	0.8473
8	9.79	0.9870	81	84.92	0.8453
9	11.00	0.9856	82	85.76	0.8433
10	12.21	0.9842	83	86.60	0.8413
11	13.41	0.9828	84	87.44	0.8393
12	14.61	0.9814	85	88.27	0.8373
13	15.80	0.9800	86	89.09	0.8352
14	16.99	0.9786	87	89.90	0.8332
15	18.18	0.9772	88	90.71	0.8311
16	19.36	0.9758	89	91.51	0.8291
17	20.54	0.9744	90	92.31	0.8270
17.85	21.55	0.9732	91	93.10	0.8249
	Immiscible		92	93.89	0.8229
64.17	69.97	0.8792	93	94.67	0.8208
65	70.74	0.8775	94	95.45	0.8188
66	71.67	0.8756	95	96.22	0.8167
67	72.59	0.8737	96	96.99	0.8147
68	73.51	0.8716	97	97.76	0.8127
69	74.42	0.8696	98	98.52	0.8106
70	75.32	0.8675	99	99.27	0.8085
71	76.21	0.8655	100	100.00	0.8063
72	77.10	0.8634			

TABLE II—TEMPERATURE CORRECTION

(Change in specific gravity per degree centigrade)

Strength Alcohol Per cent	Correction
10	0.00035
16	0.00044
Immiscible	
65	0.00077
70	0.00077
80	0.00077
90	0.00077
100	0.00077

SECONDARY BUTYL ACETATE—This compound was made by refluxing 1 mol of secondary butyl alcohol with 1 mol of acetic anhydride until the reaction was complete. After washing with water, neutralizing with sodium carbonate, and drying over calcium chloride, the ester distilled at 112.2° C. and 760 mm. Norris and Green report a boiling point of this ester at 111.5° to 112° C. at 744 mm. The specific gravity of the ester obtained by the writers was 0.8701 at 20°/4° C.

AZEOTROPIC MIXTURE OF SECONDARY BUTYL ALCOHOL AND SECONDARY BUTYL ACETATE—The mixture boiled at 99.60° C. at 758 mm. and consisted of 86.3 per cent of secondary butyl alcohol and 13.7 per cent of the ester by weight. Its specific gravity at 20°/4° C. was 0.8137. It possessed a characteristic ester odor.

SECONDARY BUTYL CHLORIDE, 2-CHLORBUTANE—This compound was made in the same manner as isopropyl chloride and the reaction proceeded very easily. The boiling point of the chloride was 68° C.,[7] at 760 mm. It had a pleasant odor and was a good solvent for fats and waxes.

SECONDARY AMYL ALCOHOL, 2-PENTANOL

This was fractionated from a mixture containing the amyl alcohol together with some water and other alcohols. In this way a large fraction boiling between 118° and 120° C. was collected. This was refractionated until a constant boiling point of 119.2° C.[8] at 760 mm. was attained. This alcohol had a specific gravity of 0.8088 at 20°/4° C.

At 20° C., 100 grams of secondary amyl alcohol dissolved 11.2 grams of water and 100 grams of water dissolved 4.2 grams of the alcohol.

TABLE III—SPECIFIC GRAVITY OF SECONDARY AMYL ALCOHOL-WATER MIXTURES AT 20°/4° C.

Per cent by Weight	Per cent by Volume	Specific Gravity
89.8	91.67	0.8299
90	91.76	0.8295
91	92.59	0.8275
92	93.43	0.8255
93	94.26	0.8235
94	95.09	0.8214
95	95.92	0.8193
96	96.75	0.8172
97	97.57	0.8151
98	98.38	0.8130
99	99.19	0.8109
100	100.00	0.8088

SECONDARY AMYL CHLORIDE, 2-CHLORPENTANE—This compound was made in the same manner as isopropyl chloride and secondary butyl chloride. It boiled at 96° C.[9] at 760 mm. It also had a sweet odor and was a good solvent for fats and waxes.

SECONDARY HEXYL ALCOHOL, 2-HEXANOL

This alcohol was fractionated from a mixture of higher alcohols. A boiling point of 139.4° to 139.6° C.[10] was obtained. This is within 0.5 degree of the boiling points given in two of the three papers referred to. The alcohol had a specific gravity of 0.8159 at 20°/4° C.

ALCOHOLS HIGHER THAN HEXYL

After the removal of all the alcohols up to and including secondary hexyl from the mixture obtained in the alcohol process, there remains an oily liquid which contains alcohols still higher than those already described. From this residual liquid have been isolated two alcohols with the characteristics of secondary heptyl (2-heptanol), and secondary octyl alcohol (2-octanol). The properties of these two alcohols have not yet been definitely determined and further work is in progress.

HIGHER ALCOHOLS IN ORGANIC SYNTHESES

All the alcohols described here are now available in commercial quantities, with the exception of the hexyl, heptyl, and octyl. While they may be used as solvents, it is apparent to the organic chemist that the availability of these hitherto very rare alcohols opens up an extensive field for their use in organic syntheses. While only a few derivatives have been mentioned in this paper, several others have been prepared. It is probable that some of these alcohols or their derivatives may find use in cosmetics and pharmaceutical preparations.

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[7] Estreicher, *Ber.*, **33**, 438 (1901); Norris and Green, *Am. Chem. J.*, **26**, 307 (1901).

[8] Wagner and Saizew, *Ann.*, **179**, 319 (1875); Bieloboubek, *Ber.*, **9**, 925 (1876).

[9] Przewalski, *Chem. Zentr.*, **1909**, II, 793; Wagner and Saizew, *Ann.*, **179**, 321 (1875).

[10] Ponzio, *Gazz. chim. ital.*, **31**, I, 404 (1901); Sabatier and Senderens, *Compt. rend.*, **137**, 302 (1903); Zelinsky and Przewalski, *Chem. Zentr.*, **1908**, II, 1855.

Registration at Milwaukee

Arkansas	4	Massachusetts	34	Pennsylvania	45
Connecticut	8	Michigan	29	Rhode Island	5
California	5	Mississippi	1	South Dakota	1
Colorado	4	Missouri	17	Tennessee	4
Delaware	5	Montana	1	Texas	3
Georgia	3	Maine	1	Utah	1
Illinois	179	Nebraska	6	Virginia	3
Indiana	33	New Jersey	20	West Virginia	6
Iowa	27	Nevada	1	Washington	4
Kansas	3	New York	59	Wisconsin	192
Kentucky	2	New Hampshire	2	Washington, D. C.	32
Louisiana	6	North Dakota	2	Wyoming	1
Maryland	6	Oregon	3	New Mexico	1
Minnesota	32	Ohio	59	Canada	2

Guests	94
TOTAL REGISTRATION	946

Some Factors Which Affect the Plasticity of a Paint[1]

By Eugene C. Bingham and Alfred G. Jacques

LAFAYETTE COLLEGE, EASTON, PA.

It is practicable to express quantitatively the effects produced upon a paint by long continued grinding, by changing the concentration of pigment, by adding soaps, water, mineral oil, or deflocculating agents, etc. Since the yield value and mobility are independent properties, these factors affect now one of these properties, then the other, and sometimes both simultaneously. This independence and the occasionally prodigious magnitude of the effects enhance the importance of the plasticity method.

EARLIER work by Booge, Bingham, and Bruce[2] proved that when two paints are carefully prepared under supposedly identical conditions so as to be identical in other properties, the plasticities of the two paints may be considerably different. This work makes it highly desirable to conduct an intensive study of the factors which influence the plasticity.

CONDITIONS OF GRINDING

An Abbé ball mill revolving at 88.5 r. p. m. was used as in a previous investigation. The writers' effort has been confined to a study of the changes in plasticity with the time of grinding. Paint B was made to contain 65 per cent by weight of Gold Seal Bechton White Lithopone and 35 per cent of acid-refined linseed oil. The oil was first added, the pigment then stirred in, and finally the pebbles were added. The paint samples were removed periodically, evacuated, and measured with the Bingham and Green plastometer.

A second paint, C, was made with the same ingredients but with 60 per cent of lithopone and 40 per cent of oil. In this case only one-half of the pigment was added during the first half hour of grinding. The remainder was added in four portions with 3 minutes of grinding between each addition. The time of grinding was then reckoned from the time of the last addition.

TABLE I—CHANGE IN PLASTICITY OF A PAINT DURING GRINDING

Time of Grinding Hours	Mobility	Yield Value Dynes Sq. Cm.
Paint B, 65 per cent lithopone and 35 per cent acid-refined linseed oil Density = 1.885, temperature = 25° C., capillary No. 10[3]		
22.6	0.38	210
31	0.38	110
39	0.36	100
55	0.31	105
63	0.26	115
71	0.22	110
Paint C, 60 per cent lithopone and 40 per cent acid-refined linseed oil Density = 1.742, temperature = 25° C., capillary No. 13		
8	0.62	250
16	0.64	200
24	0.61	110
32	0.63	90
41	0.62	80
49	0.60	85
57	0.56	90

The method of adding the ingredients with Paint *C* is a decided improvement, for during the first part of the mixing the paint is stiff, with high yield value and low mobility, as will be seen later, and the ball mill may cease to function as a mixer. It is desirable, therefore, to have the concentration of pigment much lower at the start than later when the oil is thoroughly incorporated. It has been found experimentally that, even after several hours of attempted mixing, the paint may be so inhomogeneous that on subjecting it to shear in the plastometer the more mobile portions will flow out through the capillary, so that the paint remaining in the plastometer becomes continually stiffer. Needless to say, it is impossible to obtain consistent values during this stage in the mixing.

A summary of the data obtained from Paints B and C is given in Table I.

The results prove that the yield value falls off rapidly as the grinding proceeds and reaches a constant value after a long time, much longer than was at first supposed, which under the conditions here employed is about 30 hours. The mobility increases at first slightly and then falls off. The maximum was reached in the writers' experiments in about 30 hours.

Bingham, Bruce, and Wolbach[4] ground a 65 per cent lithopone paint with acid-refined linseed oil for 16 hours, and obtained a yield value of 146 and a mobility of 0.36. They diluted this paint down to a composition of 60 per cent lithopone and 40 per cent oil, and obtained a yield value of 108 and a mobility of 0.62. The mobilities obtained by the writers agree fairly well with those of Bingham, Bruce, and Wolbach, but their yield values are considerably higher than the final yield value obtained by the writers, although not so high as the first values obtained. It is noted that the first yield value observed after many hours of grinding is more than 100 per cent higher than its final value.

TABLE II—CHANGE OF PLASTICITY WITH CONCENTRATION—25° C.

Weight Percentage of Lithopone	Mobility Observed	Mobility Calculated	Yield Value Observed	Yield Value Calculated
Paint F, Bechton White Gold Seal Lithopone of density 4.30, suspended in mineral oil containing 2 per cent of oleic acid, density 0.8751				
65.0	0.46	0.54	1010	980
62.5	0.53	0.60	810	840
60.0	0.64	0.66	720	710
55.0	0.78	0.78	430	440
50.0	0.96	0.90	280	170
45.0	1.03	1.02	230	0
35.0	1.30	1.27	115	..
25.0	1.63	1.51	95	..
15.0	1.78	1.75	40	..
0.0	2.11	2.11	0	..
Paint G, Bechton White Gold Seal Lithopone of density 4.30, suspended in a mixture of equal parts by weight of mineral oil and acid-refined linseed oil, density 0.9001				
65.0	0.43	0.49	970	970
62.5	0.54	0.57	820	810
60.0	0.63	0.64	650	650
55.0	0.75	0.79	315	320
50.0	0.93	0.93	270	0
45.0	1.09	1.08	120	..
35.0	1.42	1.37	40	..
25.0	1.67	1.66	20	..
15.0	1.96	1.95	0	..
0.0	2.40	2.40	0	..

CONCENTRATION OF THE DISPERSE PHASE

Bingham, Bruce, and Wolbach[4] found simple relations when the yield values and mobilities of paints of different concentrations were measured. In their experiments only a single series of paints was obtained by dilution; hence, it was very desirable to confirm and extend their work and to determine whether similar results would have been obtained by direct grinding of samples instead of by dilution.

In order to use vehicles which are as widely different as possible, the writers have used a neutral mineral oil contain-

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[1] Presented before the Division of Physical and Inorganic Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] *Proc. Am. Soc. Testing Materials*, **22**, II, 420 (1922).

[3] *Ibid.*, **22**, 446 (1922).

[4] *J. Franklin Inst.*, **195**, 303 (1923).

ing 2 per cent by weight of oleic acid for Paint F and a mixture of neutral mineral oil with an equal weight of acid-refined linseed oil for Paint G. Both paints were ground for 32 hours and other concentrations obtained by dilution. The results are summarized in Table II.

These results are exactly similar to those of Bingham, Bruce, and Wolbach in the following respects:

1—The yield value-concentration curve is linear at the high concentrations, indicating that a zero yield value at a definite concentration of 48 per cent by weight in Paint F and 50 per cent by weight in Paint G might be expected as compared with a concentration of 43 per cent by weight obtained by Bingham, Bruce, and Wolbach.

2—The yield value-concentration curves invariably depart from linearity at low concentrations, so that every concentration of paint, no matter how small, shows a yield value. The pseudo-plastic condition[5] in paints therefore seems to be quite well established, even though it has not as yet been explained. It is not always easy to measure the efflux satisfactorily in the pseudo-plastic mixtures, but the values of the yield values seem to lie on a smooth curve.

3—The mobility-concentration curve is quite positively linear, pointing to a concentration of zero mobility of 81 per cent by weight for Paint F, 80.5 per cent for Paint G, as against 79.6 per cent by weight in the paint studied by Bingham, Bruce, and Wolbach.

This concentration of zero mobility would seem to be related to the volume of cubical close-packing,[6] which for equal spheres is 52.4 per cent by volume. It would appear that this concentration of zero mobility ought to be the same for any given disperse phase. independent of the dispersion medium. In the three paints studied the volume concentration of zero mobility for lithopone turns out to be 46.4 per cent by volume for Paint F, 46.4 per cent by volume for Paint G, and 45.6 per cent by volume for paint studied by Bingham, Bruce, and Wolbach. This is very satisfactory agreement, the average value being close to 46.1 per cent by volume. That this value is so much less than the 52.4 per cent derived mathematically for equal spheres, may provisionally be attributed to the irregular shapes of the particles of the lithopone.

The mobilities of the three paints may be represented by the empirical formulas

Paint F, $\mu = \varphi (1 - 1.15\, n)$
Paint G, $\mu = \varphi (1 - 1.22\, n)$
Paint studied by Bingham, Bruce, and Wolbach, $\mu = \varphi (1 - 1.26\, n)$

where φ is the fluidity of the medium, and n is the fraction by weight of the disperse phase. It seems probable that the mobility of the suspension is determined by the fluidity of the medium, and one other factor which may be described as the free volume of the dispersion medium, in analogy with the free volume with which we have become familiar in pure liquids. The theory leads to a formula similar to that above except that the concentrations are by volume instead of by weight. This important peculiarity is as yet unexplained.

The mobilities as calculated by the foregoing formulas for Paints F and G are given in Table II, and the agreement between the observed and calculated values is very good.

The concentration of zero yield value as given above for Paints F and G is the same within the experimental error. This value is slightly higher than that obtained by Bingham, Bruce, and Wolbach. The concentration of zero yield value is affected by the size of particles of the disperse phase, but the yield value is very sensitive to the adhesion between the disperse phase and the dispersion medium, so that the approximate identity in these very diverse paints is remarkable. For example, if we compare these three paints at a 65 per cent concentration of pigment, we find that all of them have the same mobility—viz., 0.48—but the yield values are very different, 1010 for F, 970 for G, and 129 for the paint studied by Bingham, Bruce, and Wolbach. It therefore seems probable that the concentration of zero yield value is independent of the fluidity of the medium or of its adhesion to the pigment. It may therefore be solely dependent upon the individual particles.

It may be noted that the yield value-weight concentration curve departs from linearity at very different yield values in the different paints—viz., 400 dynes per sq. cm. for Paint F, 310 for Paint G, and 35 for the paint of Bingham, Bruce, and Wolbach. But the concentration in which this departure from linearity takes place is nearly the same, being 55 per cent for F, 55 for G, and 50 for the paint of Bingham, Bruce, and Wolbach.

The equations of the yield value-weight concentration curves are $f = 53.6\,n - 2510$ for Paint F, and $f = 66\,n - 3310$ for Paint G. The agreement between the observed and the calculated values is given in the last column of Table II.

PARTICLE SIZE

A few qualitative experiments seemed desirable to exhibit the effect of particle size on the yield value and mobility. For this purpose silica, normally used as a paint filler and known to have particles of large size as compared with the particles in lithopone, was ground in acid-refined linseed oil to contain 65 per cent by weight of silica and measured on the plastometer, at 25° C. The yield value was found to be 25 dynes per sq. cm., which is very much less than the yield value of 129 found by Bingham, Bruce, and Wolbach for the same concentration of lithopone. The mobility of the silica is 0.165, which is considerably less than the mobility of the same concentration of lithopone, 0.441. But the volume occupied by the two pigments is very different at the same weight concentration. We shall now therefore make the comparison at the same volume concentration. Assuming 2.30 as the density of the silica, the silica occupies 42.7 per cent by volume. This volume percentage of lithopone corresponds to a 75.7 per cent pigment by weight. This paint would have a mobility of 0.12 as calculated by formula and a yield value of 194. The mobilities are now nearly the same, and the yield value of the silica is 50 per cent higher than that of the lithopone. This small difference can be accounted for in a variety of ways, and is surprisingly small.

FLUIDITY OF MEDIUM

It has already been proved that temperature affects the mobility in the same ratio as it affects the fluidity of the medium, and that it does not affect the yield value. This conclusion is so important and so inherently improbable that it seemed desirable to suspend the same pigment in two oils of widely different fluidity, for which purpose blown linseed oil and lithopone have been used to compare with the lithopone paint in acid-refined linseed oil. A 35 per cent paint gave a mobility which remained constant after 7 hours of grinding, so that four successive samples gave the closely agreeing mobilities 0.0200, 0.0204, and 0.0198. The yield values read were also in good agreement, but the yield value is almost negligible, having an average value of 7 dynes per sq. cm. The 35 per cent of lithopone suspended in acid-refined linseed oil studied by Bingham, Bruce, and Wolbach, had a yield value of 7.7 and a mobility of 1.40. Therefore, the conclusion that the yield value is independent of the fluidity of the oil seems justified; but, whereas this statement is probably true, there are factors which have not yet been considered which very greatly influence the yield value and there-

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[5] THIS JOURNAL, 14, 1014 (1922).

[6] Bingham, "Fluidity and Plasticity," p. 228.

fore complicate the case. Thus, linseed oil paint has been used to compare with a blown linseed oil paint on the general assumption that they would be more nearly alike than would blown oil and mineral oil. But it is noted that 35 per cent lithopone in mineral oil with 2 per cent oleic acid gave a yield value of 115 and in a mixture of mineral and linseed oil a yield value of 40, although the fluidities of the three oils were not very different; hence, the chemical composition of the oil affects the yield value in a high degree. In the foregoing example equal *volume* compositions have been compared, but no new relationships are brought out.

The ratio between the mobilities of the acid-refined linseed oil paint and the blown linseed oil paint is 1.40:0.02 = 70, whereas the ratio between the fluidities of the oils is 2.42: 0.048 = 50. The two numbers are of the same order of magnitude, but the mobility of the blown oil paint is less than one would expect, for which no explanation has yet been found.

POLAR COLLOIDS IN SUSPENSION MEDIUM

Soaps are sometimes added to paints in order to give "false body." Just what they do is a matter of interest. The writers have experimented with zinc stearate and aluminium stearate.

When aluminium stearate is heated in linseed oil, it apparently dissolves but forms a stiff jelly or grease on cooling. The experiment was made of substituting part of the lithopone in a 55 per cent paint by weight with aluminium stearate up to nearly one per cent.

TABLE III—EFFECT OF ADDING ALUMINIUM STEARATE ON THE PLASTICITY OF A 55 PER CENT LITHOPONE IN ACID-REFINED LINSEED OIL PAINT

Aluminium Stearate Per cent	Mobility	Yield Value Observed	Yield Value Calculated
0	0.788 (B., B., and W.)	61.5(B., B., and W.)	61.5
0.25	0.679	250	249.5
0.65	0.697	550	550.3

The added material has produced a comparatively slight decrease in the mobility, but a very great increase in the yield value, which in the low concentrations is directly proportional to the concentrations. The last column in the table gives the values calculated by means of the linear formula

$$f = 752\, n + 61.5$$

DEFLOCCULATING AGENTS IN SUSPENSION MEDIUM

The attempt was made to grind 30 per cent by weight of lithopone in pure mineral oil. In spite of the low concentration of pigment, the grinding was very difficult, the paint being very pasty, and even after 48 hours of grinding measurements of the plasticity were difficult to make. The mobility was not peculiar, being about 1.0, but the yield value was extremely high—approximately 1090. But on adding as little as 0.2 per cent of oleic acid the yield value was reduced by 81 per cent, and 2.0 per cent reduced the yield value to a negligible quantity. During this extraordinary change in the yield value the mobility remained the same to within the experimental error.

It was proved by means of the microscope that the action of the oleic acid was one of deflocculation. It was also proved that the action was not due to the oleic acid acting as an electrolyte, for turpentine, which is a nonelectrolyte, has a very pronounced effect as a deflocculating agent, 1.5 per cent of it reducing the yield value to the extent of 92 per cent, and 3.0 per cent to a negligible quantity.

Stearic acid thinned down a paint, evidently lowering the yield value, but difficulty was encountered in getting consistent measurements. It would be worth while to prepare paints with a much higher yield value, in order to ascertain whether higher concentrations of the deflocculating agent than are required to furnish a layer one molecule deep over the particles would be effective in lowering the yield value.

That a 50 per cent mixture of linseed oil with mineral oil gave a yield value in a 65 per cent paint by weight of 970 as compared with 128.9 in straight linseed oil, points to the conclusion that even 50 per cent of linseed oil is not sufficient to completely disperse the pigment. The linseed oil had an acid number of 0.88.

MOISTURE

It is well known that moisture in a paint has important effects on its plasticity, but apparently no one has attempted to measure these effects quantitatively. Paint C, made up to contain 60 per cent by weight of air-dried lithopone in acid-refined linseed oil, was found to have a yield value of 90 and a mobility of 0.64 after 32 hours of grinding. On adding 0.5 per cent of moisture and grinding in the ball mill, it was found that the yield value had risen to the extraordinary value of 3450 dynes per sq. cm. and the mobility had fallen to 0.142 absolute unit. In thus affecting both the yield value and the mobility, moisture seems to play a unique role most nearly resembling the action of a polar colloid. A further study is planned to find out the effect on plasticity of both smaller and larger quantities of moisture, and to determine the mechanism of the phenomenon.

OXIDATION OR POLYMERIZATION

From experiments with lithopone in acid-refined linseed oil and in blown oil, it may be stated with some confidence that the yield value will not be altered except as the adhesion between the oil and pigment is changed, but that the mobility will be changed in direct proportion to the change in the fluidity of the medium.

In the grinding experiments it was observed that the mobility fell off with long continued grinding. It appears possible that there may be two counter effects—one due to the gradual wetting and separation of the individual particles, and the other due to the oxidation or polymerization of the medium. The latter tendency would adequately explain the falling off of the mobility on long grinding while the yield value remains constant. It was thought that this could be best tested by carrying out the grinding in a more inert atmosphere, using nitrogen or carbon dioxide.

In Table I the plasticity of a 60 per cent lithopone paint in acid-refined linseed oil, ground in atmospheric air, has already been given, this being Paint C. In Table IV are given the data of Paints D and N, the first being ground in an atmosphere of carbon dioxide, and the second being ground in an atmosphere of nitrogen with 0.5 gram of anticatalyst. Otherwise, the three paints are intended to be identical.

In each case the mobility at first increases, passes through a maximum, and then falls off more and more rapidly. The maximum occurs after about 32 hours' grinding, the value of the maximum being 0.63 for Paint C, 0.64 for Paint D, and 0.60 for Paint N. At the end of 64 hours the mobility of Paint C has fallen off probably 15 per cent, Paint D in carbon dioxide some 7 per cent, and Paint N in nitrogen some 6 per cent. Thus, it does not appear that an inert atmosphere is able to prevent the change which causes the falling off in the mobility.

It may be that still other factors than oxidation and polymmerization will eventually have to come in for study. The writers suggest the possibility of moisture derived from the pigment or the atmosphere, solid material resulting from the wear of the mill, alkaline material derived from the mill, or chemical reaction between the pigment and some part of the oil.

Dissolved Gases

In the course of this work it was observed that carbon dioxide is very soluble in paint. The writers have evacuated each paint before measurement so that they would be fully comparable. Assuming oxidation or polymerization to be the only change taking place on grinding, they expected the yield value to be the same in the three paints. They were therefore surprised to find the yield value quite different in the three paints—viz., 90 in Paint C, 280 in Paint D, and 200 in Paint N. Sufficient work has not been done as yet to make it safe to hazard an explanation of this striking difference. In these experiments the materials were used in their air-dry condition, but in future experiments it will be desirable to regulate the moisture conditions much more carefully.

Temperature

Work already done has made it appear that the increase in mobility with the temperature is in direct ratio to the increase in the fluidity of the medium. Naturally, this generalization is subject to limitations, since the adhesion may change with the temperature, colloids may pass from the gel to the sol condition as the temperature is raised, etc.

Dimensions of the Instrument

All the measurements described in this paper were made on a given type of plastometer, for which changes in the length and radius of the capillary are without effect.

TABLE IV—CHANGE IN PLASTICITY DURING THE PROCESS OF GRINDING A PAINT

Time of Grinding Hours	Mobility in Absolute Units	Yield Value in Dynes per Sq. Cm.
Paint D, 60 per cent lithopone and 40 per cent acid-refined linseed oil, density × 1.742, temperature 25° C., capillary No. 10. Ground in an atmosphere of carbon dioxide		
16	0.61	340
24	0.61	280
32	0.63	280
49	0.64	280
56	0.62	270
64	0.61	280
Paint N, 60 per cent lithopone and 40 per cent acid-refined linseed oil, density × 1.747, temperature 25° C., capillary No. 10. Ground in an atmosphere of nitrogen		
6	0.51	310
22	0.58	230
34	0.59	210
40	0.60	200
48	0.57	150
52	0.57	95
56	0.55	100
70	0.56	150
80	0.53	110

Conclusions

1—As the grinding of a pigment in oil progresses, the yield value at first decreases but after 30 hours becomes constant. The mobility under the same conditions at first increases, passes through a maximum, and then decreases more and more rapidly. The maximum occurs after about 30 hours in these experiments.

2—On measuring different concentrations of pigment suspended in oil, the yield value-weight concentration curve is found to be linear except at low concentrations, thus confirming the findings of Bingham, Bruce, and Wolbach. All concentrations exhibit a yield value. The concentration of zero yield value is apparently independent of the nature of the medium.

The mobility-weight concentration curve is also linear and the concentration of zero mobility is apparently independent of the nature of the vehicle. The theory would lead one to expect that simpler relations would be found when using volume concentrations, but this is not the case, for which no explanation has yet been given.

3—Silica and lithopone have very different plasticity at the same weight concentration. When they are compared at equivalent volume percentages, however, the mobilities are nearly the same and the yield values are not very different. This fact is the more striking since the particle size in the two pigments is so different.

4—Comparing blown oil with acid-refined linseed oil at the same concentration of pigment, the effect of the fluidity of the medium is shown. The mobility falls off in presumably the same ratio as the fluidities of the oil, but the yield value is independent of the fluidity of the oil.

5—Polar colloids—as, for example, aluminium stearate—have very slight influence on the mobility, but they have an extraordinary effect in raising the yield value.

6—It is difficult to grind a pigment into pure mineral oil having the same fluidity as linseed oil and it is still more difficult to make a satisfactory plasticity determination on the resulting suspension. However, 0.2 per cent of oleic acid deflocculates the suspension and lowers the yield value about 80 per cent, while the mobility remains unchanged.

7—Moisture exerts a prodigious effect on the plasticity of paint, 0.5 per cent of moisture raising the yield value from 90 to 3450, and at the same time reducing the mobility to one-fourth of its former value.

8—Oxidation and polymerization affect the fluidity of an oil, so we should expect the mobility to be affected. It was thought that the fall in the mobility on long grinding might be attributable to one of these causes, but grinding in an atmosphere of nitrogen only prevented it, partially. A paint ground in an atmosphere of carbon dioxide has a yield value three times as high as when ground in the air.

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Oxygen and Oxygenated Air in Metallurgical Processes

Revolutionary changes in the metallurgy of iron, by which production costs should be materially decreased and quantities of low-grade ore and smelting fuels now considered worthless be made available as the result of the use of oxygen and oxygenated air in blast furnace practice, are suggested in a report recently made to the Department of the Interior by a committee appointed by the Bureau of Mines to study the problem.

In the past it has been necessary in the production of 1 ton of pig iron to pass 3 tons of inert nitrogen through the blast furnace, resulting in serious heat and metal losses. The elimination of such losses by the substitution of oxygen, or a mixture of oxygen and air, has long been considered, but has not been put into practice on account of the inability to produce oxygen in quantities at sufficiently low cost to make such application industrially possible.

In view of the many recent developments in oxygen manufacture, and considering the increasing cost and decreasing quality of the nation's raw materials, the Bureau of Mines appointed an advisory committee, of which M. H. Roberts of New York is chairman, to study the problem of the application of oxygen or oxygenated air to metallurgical and allied processes. This committee has made a thorough survey of the existing processes for the manufacture of 99 per cent oxygen, and finds that the oxygen industry is now able to make plants for supplying large quantities of oxygen to metallurgical industries at low cost.

The data collected by this committee indicate that the production and utilization of cheap oxygen should also accomplish great economies in the metallurgy of zinc. It is believed that similar economies can be effected in the metallurgy of copper, and in fact in all branches of nonferrous metallurgy.

The committee has developed plans for experimentally determining the effects of oxygen-enriched air upon the operation of the blast furnace, and it is recommended that these plans be put into effect as the first step of an extended research as to the general applicability of oxygen to metallurgy. The knowledge that German industrial concerns are working actively on the application of oxygenated air to metallurgical processes has greatly concerned American iron and steel interests, and the industry is making insistent demands for research work of this nature.

Insoluble Phosphoric Acid in Acid Phosphates and Fertilizers[1]

Some Sources of Error in Its Determination

By W. R. Austin

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It is important to observe the precaution of washing the sample with water up to the volume of 250 cc. as prescribed in the official method, and also to select rapid filtering funnels so that the washing may be done in about 20 to 30 minutes.

There is an important relation between the Fe_2O_3 and P_2O_5 removed by thorough washing—as the percentage of Fe_2O_3 removed by washing is increased the percentage of insoluble P_2O_5 decreases.

While the same care should be exercised in making the ammonium citrate exactly neutral, as prescribed by the official method, yet moderate differences in the ratio of ammonia to citric acid make relatively little difference in the results for insoluble as compared to the importance of careful preliminary washing.

THE purpose of this article is to emphasize certain sources of discrepancies in the determination of insoluble P_2O_5, particularly those arising from incomplete preliminary washing of the sample, and the relative effect of using various solutions of ammonium citrate solution.

The official method of the Association of Official Agricultural Chemists prescribes: "Place 2 grams of the sample on a 9-cm. filter, wash with successive small portions of water, allowing each to pass through before adding more, until the filtrate measures about 250 cc. ***." This precaution of washing the sample to 250 cc. has not been observed by some analysts, resulting in many cases in wide discrepancies.

In the case of one sample of acid phosphate made from Tennessee phosphate rock, on which considerable collaborative analytical work was done, the importance of thorough preliminary washing was strongly emphasized. One group of analysts, accustomed largely to handling acid phosphate made from Florida rock, reported consistently about 0.75 per cent insoluble P_2O_5, while others, more familiar with acid phosphate made from Tennessee rock, found about 0.40 per cent insoluble. After a careful investigation, including exchange of samples of ammonium citrate, etc., it was developed that the trouble was entirely in the preliminary washing. Those who were in the habit of washing the sample at first with only three or four washings with water reported the highest results. After this investigation further determinations were made on the same sample, with a close agreement averaging, for ten analysts, 0.36 per cent, six of the number reporting 0.37 per cent. This work led to the following:

Sample A—Acid phosphate, after different periods of curing made from Tennessee rock (rock containing about 2.4 per cent Al_2O_3 and 2.7 per cent Fe_2O_3)

Period of Curing		Per cent Insoluble P_2O_5: Washed to 100 Cc. (4 to 5 Washings)	Per cent Insoluble P_2O_5: Washed to 250 Cc. (10 Washings)
1	day	2.19	1.96
10		0.94	0.62
4	weeks	0.48	0.35
6		0.49	0.31
10		0.50	0.38
12		0.65	0.45
14		0.48	0.33

Sample B—Acid phosphate, 6 months old, varied size of filter papers, also volume of water in washing (prior to treatment with ammonium citrate)

Volume of Washing Cc.	Per cent Insoluble P_2O_5: 11-Cm. Filter	Per cent Insoluble P_2O_5: 9-Cm. Filter
100	0.30	0.27
150	0.25	0.15
200	0.15	0.15
250	0.15	0.15

Sample tested directly, no preliminary washing with water—0.30 per cent insoluble.

Separate portions of Sample B were similarly washed, as above, and the Fe_2O_3 remaining in the washed residue determined.

	Per cent Fe_2O_3
Unwashed sample	2.35
After washing to 100 cc., 9-cm. filter	2.30
After washing to 150 cc., 11-cm. filter	2.30
After washing to 200 cc., 9-cm. filter	2.10
After washing to 250 cc., 9-cm. filter	2.05

Many analysts prefer the 11-cm. filter to avoid loss in washing when churning up the sample with the stream of water. There is apparently an advantage, in the case of some samples, in using a 9-cm. filter, since a greater number of washings is required to give the 250 cc. than when the 11-cm. filter is used. In most cases, however, ten washings on a 11-cm. filter using about 25 cc. each time were sufficient.

It has been found with some samples that the percentage of insoluble after washing to 250 cc. is quite appreciably lower than when washing to 150 cc. There seems to be an important relation between such results and the Fe_2O_3—the greater the number of washings the more Fe_2O_3 combined with P_2O_5 is washed through resulting in lower results for insoluble.

Several samples of acid phosphate were next taken, washed to different volumes, and the percentage insoluble P_2O_5 and Fe_2O_3 determined.

		Per cent Insoluble			
	Unwashed	100 Cc. (4 Washings)	150 Cc. (6 Washings)	200 Cc. (8 Washings)	250 Cc. (10 Washings)
Sample C—Acid phosphate 1 day old (Tennessee rock)					
P_2O_5	2.26	2.19	2.15	2.05	1.96
Fe_2O_3 in washed residue	2.05	2.00	2.00	1.90	1.80
Fe_2O_3 after citrate treatment	..	0.40	0.40	0.40	0.25
Sample D—Acid phosphate, 8 months old (Tennessee rock)[a]					
P_2O_5	0.32	0.29	0.20	0.14	0.12
Fe_2O_3 in washed residue	2.10	2.10	2.00	1.90	1.83
Fe_2O_3 after citrate treatment	0.43	0.40	0.38	0.35	0.28
Sample E—Double superphosphate (45 per cent available P_2O_5)[a]					
P_2O_5	..	2.40	2.25	..	2.14
Fe_2O_3 in washed residue	..	1.50	1.40	..	1.20
Sample F—Acid phosphate, 1 year old (Florida rock)					
P_2O_5	..	0.24	0.18	..	0.14
Fe_2O_3 in washed residue	..	1.20	1.10	..	1.06
Sample G—Acid phosphate, 1 week old (Florida rock)					
P_2O_5	..	0.55	0.42	..	0.38
Sample H					
Average results for insoluble P_2O_5 on eight samples of mixed fertilizers, containing acid phosphate, nitrogen, and potash	..	2.03	1.98	1.90	1.83

[a] The results in Samples D and E are the average reported by ten laboratories.

The importance of thorough washing of the sample with water prior to its treatment with ammonium citrate having been established, a series of tests was made to determine the effect of different solutions of ammonium citrate. Just prior to this, however, two samples of acid phosphate had been sent to twelve laboratories together with some of a solution of neutral ammonium citrate, with the request to determine insoluble P_2O_5 using this citrate solution and also using their own. The average of the twelve tests on the ammonium citrate solution sent from this laboratory showed a ratio of ammonia

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[1] Presented before the Division of Fertilizer Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922. Received August 17, 1923.

to citric acid of 1:3.759. The average results for insoluble from the twelve laboratories follow:

		Per cent Insoluble Minimum	Maximum	Av.
	Sample I—Well-cured acid phosphate			
Citrate solution:	Other laboratories............	0.08	0.29	0.18
	Author's laboratory	0.06	0.29	....
	Sample J—16 per cent acid phosphate			
Citrate solutions:	Other laboratories............	0.73	0.95	0.88
	Author's laboratory	0.74	0.95	....

Nine laboratories reported results in close agreement on the first report, and after further work and observing the precautions of thorough preliminary washing, all agreed within 0.05 per cent. It was found that the difference was not due to ammonium citrate solutions, since the laboratory reporting the lowest results, likewise the one reporting the highest results, found the same with both solutions.

Sample K was then prepared and portions sent to ten laboratories. This was a sample of mixed fertilizer containing about 2 per cent NH_3, 10 per cent available P_2O_5, and 10 per cent K_2O. The results reported varied from 1.00 to 1.21 per cent, averaging 1.08 per cent.

In order to determine the effect of using a neutral solution of ammonium citrate as compared with solutions containing excess ammonia and others containing excess citric acid, the foregoing tests (Samples *K* to *O*) were made.

Per cent Insoluble

	Using Neutral Citrate Volume Preliminary Washing 100 Cc.	150 Cc.	250 Cc.	Using Neutral Citrate Plus Ammonia or Citric Acid (Preliminary Washing 250 Cc.) Containing Excess Ammonia or Acid as Follows	0.5%	1.0%	2.5%	5.0%	10.0%
Sample *K*—Mixed fertilizer, 2:10:10..........	1.20	1.12	1.09	NH_4OH	1.08	1.10	1.10	1.11	1.11
				Citric acid	1.08	1.02	1.00	0.95	0.95
Sample *L*—16% Acid phosphate from Florida rock	0.30	0.25	0.25	NH_4OH	0.25	0.25	0.17	0.16	0.16
				Citric acid	0.23	0.21	0.20	0.18	0.16
Sample *M*—Acid phosphate from Tennessee rock	0.37	0.30	0.25	NH_4OH	0.37	0.27	0.27	0.28	0.27
				Citric acid	0.25	0.20	0.15	0.14	0.12
Sample *N*—16% Acid phosphate plus lime.....	3.77	3.65	3.61	NH_4OH	3.62	3.62	3.67	3.97	4.12
				Citric acid	3.64	3.59	3.51	3.44	3.33
Sample *O*—Mixture acid phosphate and cottonseed meal..............................	....	....	0.25	NH_4OH	....	....	0.23	0.25	....
				Citric acid	....	....	0.23	0.21	....

Similar tests were made on a mixture of equal parts of acid phosphate and bone meal, when the effect of adding ammonia or citric acid to a neutral solution of ammonium citrate was more marked.

It was found important to select a long-stem (5 to 6 inches), 60-degree funnel for the preliminary washing, and with a carefully fitted paper the washing up to 250 cc. may be done in 20 to 30 minutes. It was further noted that when this precaution is not observed and an hour or more is required for washing, the results for insoluble are generally higher. (Some analysts add a little paper pulp or asbestos to increase rapidity of washing.)

Many other determinations were made by using different grades of filter papers, varying the temperature of the wash water, diluting before precipitation, etc., but none of these changes affected the results appreciably, especially as compared with the importance of thorough preliminary washing of the sample.

Acknowledgment

The author wishes to hereby express his thanks to H. C. Moore for many suggestions offered in this work, to those who have made many collaborative determinations, and his assistant, L. C. Smith, who has made a large number of careful determinations in the work.

An Improved Stopcock[1]

By P. H. Kollewyn

Martinez, Calif.

THIS little article is written to introduce to chemical engineers who have experienced trouble with leaking valves an improved stopcock which does not leak if properly handled. It has all the advantages of the regular stopcock, as easy adjustment, quick opening and closing, without the disadvantages of sticking and subsequent hammering or twisting off of the square top of the stem.

This stopcock was invented[2] as a result of trouble arising from the frequent replacements of valves in the acid lines of a California oil refinery. The first one was installed there in 1919 and is still in use. In Mexico this valve was used exclusively on all lines for corrosive liquids and also for steam and hot-oil lines.

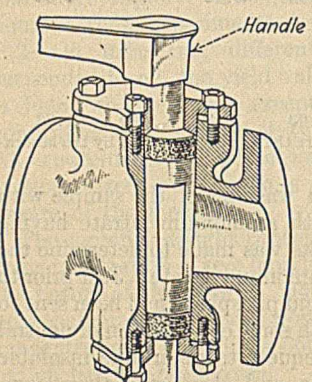

Fig. 1

The advantages of the double packed stopcock are:

Easy Installation—After the house is installed in the line the plug is put in and the top flange (see Figs. 1 and 2 showing the low- and high-pressure valves) is bolted on tightly, so tightly that the plug can hardly be moved. After this the bottom flange, which before installation was fastened snugly, is tightened, thus relieving the pressure on the plug which is taken up in the top and bottom packing. The bottom flange is tightened just enough to secure easy movement of the plug.

Easy Handling—In case the valve "sticks," due to wear, the top flange is slightly loosened and the bottom flange tightened, thus securing a very quick repair without danger of the operator breaking the stem or the house, because no force is used as hammering or twisting. This valve can be repaired without interfering with the operation.

Easy Cleaning—The two openings on both sides of the house make an effective cleaning possible without taking the valve out of the line.

Replacements of Parts—If, after long service, the plug is worn out too far, it can be easily replaced by an oversize or new plug, which means a considerable cut in costs because the housing remains in the line. The high pressure valve is very well adapted for a boiler blowoff valve. It carries an extra safety flange on top and if fitted with a diamond boring it complies with the government specifications, as it cannot be opened at once to its full extent because the plug and the house have to warm up slowly to the same temperature before the plug can be turned easily.

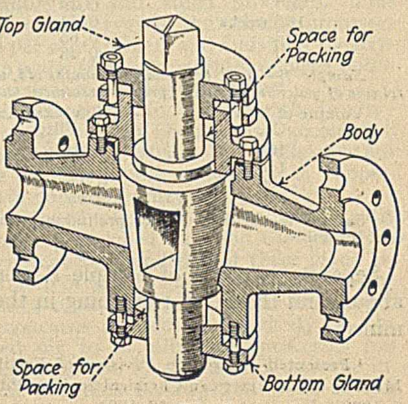

Fig. 2

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[1] Received May 2, 1923.

[2] U. S. Patent 1,370,745 (March 7, 1921).

Chemical, Physical, and Biological Properties of Bordeaux Mixtures[1]

By O. Butler

New Hampshire Agricultural Experiment Station, Durham, N. H.

In this paper it is shown that in practice three types of Bordeaux mixture are recognized—acid, neutral, and alkaline washes. The methods of preparation and chemical properties of these mixtures are briefly described and it is pointed out that as the lime content in a mixture is increased the shading action of the wash becomes more obvious and its adhesiveness increased until the ratio of cupric sulfate to calcium oxide exceeds 1:0.5 when it begins to fall. It is also shown that the rate of settlement of a Bordeaux mixture, on which much emphasis has been placed, is not in any sense a measure of adhesiveness. From the facts presented it could also be concluded that if the shadow cast by an alkaline Bordeaux mixture was injurious then a neutral mixture could be substituted and this depressing effect removed. It is also briefly pointed out that when Bordeaux mixtures are injurious at the time of application the injury produced depends both on the composition of the wash and the specific sensitivity of the organ sprayed.

LONG before the downy mildew of the grape was known in Europe the grape growers would, as soon as the fruit began to mature, daub upon the vines bordering the highways and byways a mixture composed of milk of lime and copper sulfate, the object being to prevent pilfering. The downy mildew appeared in the Gironde in 1881 and Millardet[1] noticed, in the course of perambulations in the environs of Bordeaux in 1882, that the mixture the vineyardists were in the habit of daubing upon their grape vines with a small fagot broom distinctly preserved the treated plants from the ravages of the disease. The importance of this fact did not escape him. Millardet immediately began experimenting, and on April 1, 1885, reported the results of his experiments. The mixture he used had the composition[2]

Copper sulfate	5.71 parts
Quicklime	10.71 parts
Water to make	100 parts

and was therefore thick and heavy and not suited for use in sprayers. The formula necessarily needed modification and the Bordeaux mixture proposed in 1885 was soon replaced by more fluid washes, the most radical change introduced being in the amount of quicklime used. The ratio of cupric sulfate to quicklime, which in the original wash was 1:1.87, was changed by Millardet and Gayon[3] in 1887 to 1:0.3. These authors proposed for use in general practice a Bordeaux mixture of this composition containing 3 per cent cupric sulfate, and for trial similar mixtures containing 2 per cent and 1 per cent cupric sulfate, respectively. Further modifications of the original formula were introduced from time to time by various authors, and before the close of the 19th century there were recognized in the literature three types of Bordeaux mixture—acid Bordeaux mixture, neutral Bordeaux mixture, and alkaline Bordeaux mixture.

Acid Bordeaux mixture is, strictly speaking, a wash so made as to contain a small amount of soluble copper and give a faint acid reaction. In practice, however, the mixture is usually made by adding milk of lime to a solution of cupric sulfate until an alkaline reaction is obtained, when a small amount of cupric sulfate is added, 0.1 per cent in the case of a 1 per cent Bordeaux mixture, and 0.2 per cent in the case of a 2 per cent Bordeaux mixture. Obviously, as usually prepared, acid Bordeaux mixture will not give an acid reaction, or contain soluble copper.

Neutral Bordeaux mixture is made by adding milk of lime to a solution of cupric sulfate until no soluble copper can be detected by means of potassium ferrocyanide,[4] or, more commonly, by adding milk of lime until an alkaline reaction is obtained. A Bordeaux mixture in which the ratio of cupric sulfate to quicklime is 1:0.3 falls in this group.

Alkaline Bordeaux mixture is a wash containing cupric sulfate to quicklime in a ratio of not less than 1:0.5, though mixtures containing a ratio 1:3 and 1:5 have been recently introduced.[5] The alkaline Bordeaux mixture most commonly used in the United States is a wash containing cupric sulfate and quicklime in equal amounts.

The ratio cupric sulfate to quicklime used in preparing a Bordeaux mixture has an important effect on the chemical, physical, and biological properties of the wash—is, in fact, of more importance than is commonly supposed.

CHEMISTRY OF BORDEAUX MIXTURES

According to Millardet and Gayon,[6] Chester,[7] Fairchild,[8] and the majority of writers on the subject, the reaction that takes place when cupric sulfate and milk of lime or limewater are brought together results in the formation of cupric hydroxide and calcium sulfate, calcium hydrate being also present when the limewater or milk of lime is used in excess. Millardet and Gayon[3] did, however, observe that cupric sulfate and calcium oxide would combine in the ratio of 1:0.179, which is very nearly the ratio required for the formation of the basic sulfate $5CuO.SO_3$; and Fairchild expressed the opinion that basic sulfates are at first formed when milk of lime is slowly added to a solution of cupric sulfate.

Sostegni[9] studied the reactions involved in the preparation of Bordeaux mixture, and concluded that the copper precipitate was composed of cupric hydrate, basic cupric sulfate, and a double sulfate of lime and copper.

Vermorel and Dantony[10] state that the copper is precipitated in acid Bordeaux mixtures as basic sulfates, but that in alkaline washes cupric hydrate is almost exclusively formed when the milk is poured quickly into a solution of cupric sulfate and basic sulfates where it is added very slowly.

The most comprehensive study of Bordeaux mixture has been made by Pickering. According to this author[11] the following distinct basic salts may be formed when cupric sulfate is precipitated by calcium hydrate in the form of limewater: $4CuO.SO_3$; $5CuO.SO_3$; $10CuO.SO_3$; $10CuO.SO_3.3CaO$.

These CuO.3CaO basic sulfates, omitting CuO.3CaO, which is of no particular interest to the student of Bordeaux mixture, are formed when cupric sulfate and calcium hydrate are com-

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[1] Presented before the Division of Agricultural and Food Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[*] The numbers in the text refer to the bibliography at the end of the article.

bined in the proper proportions to give the following ratios of cupric sulfate to calcic oxide: $4CuO.SO_3$, 1: 0.166; $5CuO.SO_3$, 1:0.181; $10CuO.SO_3$, 1:0.2; $10CuO.SO_3.CaO$, 1:0.269. The basic sulfates $4CuO.SO_3$ and $5CuO.SO_3$ are somewhat soluble in the mother liquor, the former to the extent of 1 part in 40,000, the latter to the extent of 1 to 2 parts per million. The other basic salts, however, are quite insoluble in the mother liquor, though, beginning with $10CuO.SO_3$, they dissolve with increasing readiness in saccharose.

When the basic sulfates are boiled, $10CuO.SO_3$ decomposes with formation of cupric oxide, but the other basic salts are not affected. None of the basic salts crystallize with age.

In practice the only basic sulfates that can be found in Bordeaux mixtures are $5CuO.SO_3$, $10CuO.SO_3$, and $10\ CuO.SO_3$, $3CaO$ either alone or mixed, according to Pickering, with a more highly basic salt the composition of which has not been determined, $4CuO.SO_3$ does not occur, since even in acid Bordeaux mixtures the ratio of cupric sulfate to quicklime will always be such that the lowest basic sulfate that could be formed would be $5CuO.SO_3$.

In neutral Bordeaux mixtures cupric oxide gradually forms on standing, but does not appear in mixtures in which the ratio of cupric sulfate to calcium oxide lies between 1:0.25 and 1:1. When, however, mixtures of these latter types are boiled, cupric oxide may or may not form, its appearance depending on the percentage strength in cupric sulfate of the mixture, as a study of Table I will show.[12]

TABLE I—EFFECT OF BOILING ON THE DEVELOPMENT OF CUPRIC OXIDE IN BORDEAUX MIXTURES

Strength of Mixture Per cent	Ratio $CuSO_4$:CaO	Cupric Oxide
2	1:1.00	Formed
2	1:0.50	
2	1:0.25	
1	1:1.00	
1	1:0.50	
1	1:0.25	
0.5	1:1.00	Not formed
0.5	1:0.50	
0.5	1:0.25	Formed
0.25	1:1.00	Not formed
0.125	1:1.00	

These data show that as soon as there is sufficient calcium hydrate in solution to give, on combining with the cupric sulfate, the basic sulfate $10CuO.SO_3.3CaO$ or $10CuO.SO_3.3CaO$ admixed with higher basic salts, no cupric oxide forms on boiling the mixture.

When first prepared the Bordeaux mixtures encountered in practice form gelatinous precipitates, which are not usually stable and change more or less profoundly, depending on the temperature, the percentage strength in cupric sulfate, and the ratio cupric sulfate to calcium oxide used. In acid and neutral Bordeaux mixtures cupric oxide gradually forms and the precipitate becomes granular; in alkaline Bordeaux mixtures the gelatinous precipitate is usually replaced by spherocrystals. If one prepares a series of Bordeaux mixtures containing 0.125, 0.25, 0.50, 1, 2, 4, and 6 per cent cupric sulfate, in which the ratio of cupric sulfate to calcium oxide is 1:1, he will find that spherocrystals will appear in all the mixtures except the 0.125 per cent wash. Bordeaux mixtures in which the ratio of cupric sulfate to calcium oxide is 1:0.5 behave similarly to 1:1 mixtures. The 0.125 per cent mixture shows little or no change with age, while in the stronger mixtures blue spherocrystals, apparently similar to those occurring in the 1:1 mixtures, appear, but more slowly than in washes of the latter type. It was found that in alkaline Bordeaux mixture cupric oxide did not always form when the wash was boiled. There is no relation between the formation of cupric oxide and the development of spherocrystals on standing. It would appear that in Bordeaux mixtures the copper salt at first formed is not stable. In acid and neutral washes it changes gradually to cupric oxide; in the alkaline washes the change is to the formation of spherocrystals irrespective of the reaction given by the copper salt when the mixture is first made. These differences are due to the limited solubility of calcium hydrate. In strong Bordeaux mixtures the copper is precipitated in the same form, but if the calcium hydrate in the form of milk of lime is used in large excess the reaction will continue until equilibrium is reached.

The crystallization of Bordeaux mixtures may be prevented by the use of a small amount of saccharose. Kelhofer,[13] who first proposed the use of saccharose for this purpose, states that the amount required is determined by the ratio cupric sulfate to calcium oxide used. For a 1 per cent Bordeaux mixture 1:1 the amount required for 50 gallons is 2 ounces. Alkaline Bordeaux mixtures containing small amounts of saccharose remain gelatinous for a number of months, but eventually cuprous and cupric oxides form.

ADHESIVENESS OF BORDEAUX MIXTURES

The adhesiveness of Bordeaux mixtures has been studied by several investigators,[14] and the subject is one of considerable practical importance.

Acid Bordeaux mixtures are less adhesive than neutral washes, and very alkaline washes are not as adhesive as mixtures in which the ratio of cupric sulfate to quicklime is 1:0.5. From the standpoint of adhesiveness there is no reason for increasing the lime content of a Bordeaux mixture beyond the amount required to give the ratio 1:0.5. The adhesiveness of a strictly neutral Bordeaux mixture prepared from limewater—that is, a mixture in which the ratio of cupric sulfate to calcium oxide is 1:0.2—is extremely poor since it is very highly gelatinous, so gelatinous that when it dries on a leaf the rate of drying of the surface exposed to the air is so much faster than that of the layer in contact with the leaf, that the tension produced causes the edges to curl to such an extent that the greater part of the mixture flakes off. A strictly neutral Bordeaux mixture is not serviceable in practice. In fact, it is rather doubtful whether any benefit is to be derived from using extremely gelatinous mixtures. What is needed is copper in a very fine state of division. For instance, if we study the rate of settlement of a 1 per cent Bordeaux mixture 1:1 made with water at 10° C., a very gelatinous mixture, with a similar mixture made with water at 30° C., a wash in which the copper is precipitated partly in granular form, we will find marked differences in their rates of settlement but no difference in their adhesiveness to Coleus leaves.

TABLE II—EFFECT OF TEMPERATURE OF WATER USED ON THE RATE OF SETTLEMENT AND ADHESIVENESS OF 1 PER CENT BORDEAUX MIXTURE 1:1

MIXTURE MADE WITH	Relative Numbers ½ Hr.	Relative Numbers 1 Hr.	Relative Numbers 2 Hrs.	Adhesiveness 10 = perfect
Water at 10° C.	6.5	22.5	66.0	7.1
Water at 30° C.	100.0	250.0	445.0	7.1

It has generally been assumed that the adhesiveness of a Bordeaux mixture was greater in slowly than in rapidly settling mixtures and better in freshly made than in mixtures that had been prepared for some time. The data in Table II show that too much importance should not be attached to the method of mixing, but, on the other hand, the opinion that a freshly made mixture is more adhesive than one that has been allowed to stand would seem to be sound in the case of Bordeaux mixtures that crystallize. The data in Table III show that a Bordeaux mixture in which the copper precipitate has assumed the crystalline form is much less adhesive than a freshly made wash.

TABLE III—RELATIVE ADHESIVENESS OF 1 PER CENT BORDEAUX MIXTURE 1:1 FRESHLY MADE AND DETERIORATED[14]

	Adhesiveness, 10 = perfect
Copper precipitate gelatinous	6.7
Copper precipitate crystalline	4.7

BIOLOGICAL PROPERTIES

PHYSICAL EFFECTS—Bordeaux mixtures are, as a simple inspection of the dried washes would show, unequally transparent, the opacity increasing as the ratio of cupric sulfate to calcium oxide approaches unity. One would therefore expect that a plant sprayed with a neutral wash would respond somewhat differently than a plant sprayed with an alkaline mixture, and, effectively, as the data in Table IV show, we find that the sprayed plant develops normally on the one hand and slightly abnormally on the other.

TABLE IV—EFFECT OF SPRAYING WITH BORDEAUX MIXTURE AND MILK OF LIME ON DRY MATTER FORMED AND TRANSPIRATION PER GRAM DRY MATTER[15]

	Dry Weight			Transpiration per Gram Dry Matter		
	Sprayed with Bordeaux Mixture		Not	Sprayed with Bordeaux Mixture		Not
VARIETY USED	1:1 G.	1:Alkaline G.	Sprayed G.	1:1 G.	1:Alkaline G.	Sprayed G.
Radish Early	0.74	0.95	0.66	27.80	25.20	24.20
Scarlet Globe	1.97	2.33	2.74	37.50	27.60	30.60
	2.67	3.10	2.92	40.73	32.39	34.84
AVERAGE...	1.79	2.12	2.10	35.34	28.39	29.88
Tomato Bonny	2.42	3.18	2.95	19.70	9.77	9.95
Best	7.59	8.47	8.43	23.82	21.83	22.06
AVERAGE...	5.00	5.82	5.69	21.76	15.80	16.00
Bean Dwarf	3.28	3.41	3.68	20.20	18.20	18.70
Horticultural	3.60	4.76	5.38	6.52	4.97	4.78
AVERAGE...	3.44	4.08	4.53	13.66	11.58	11.74

The literature is not in agreement in regard to the effect of Bordeaux mixtures on the rate of transpiration of sprayed plants, though the weight of the evidence indicates increased transpiration.[15] It has been observed by Daggar and Bonns[16] that spraying with Bordeaux mixture increases transpiration especially at night. The writer has observed that increased transpiration is noticeable especially under conditions favorable for radiation and that Bordeaux mixtures are opaque to the infra-red. We would therefore expect, other things being equal, sprayed plants to transpire more actively at night than nonsprayed plants. However, it should be noted that increased transpiration of sprayed plants at night does not of itself account for the effect of Bordeaux mixtures, because all Bordeaux mixtures cause increased transpiration to some degree but they do not all affect plants in a similar manner. The response of sprayed plants is to be attributed to difference in translucency of the mixtures to the solar spectrum. Schrander[17] was the first to advance the view that the action of Bordeaux mixture on plants was one of shade. Bordeaux mixtures, however, while not equally opaque to luminous radiations, do not show *inter se* quite so marked differences as the behavior of the sprayed plants indicates that they should. The response obtained is not due to shade, using the term in its ordinary acceptance, but to different degrees of athermancy of the washes to the spectrum. When the spectrum as a whole is considered 1 per cent, alkaline Bordeaux mixture is much more opaque than neutral Bordeaux mixture, and there is concordance between the physical properties of the washes and the response of plants sprayed with them.

CHEMICAL EFFECTS—When we study the response of sprayed plants to the chemical action of Bordeaux mixtures we find rather a complex situation—we have to consider the effect of the mixture at the time of application, and the effect of the mixture after it has dried. The effect of Bordeaux mixtures after they have dried seems to be due entirely to the sensitiveness of the plant to soluble copper. The action of Bordeaux mixtures at the time of their application depends, on the other hand, on the type of mixture used, on the kind and variety of plant sprayed, and on the nature and age of the organ sprayed. In the *grape*, when Bordeaux mixtures are injurious it will be found that alkaline washes are more injurious than neutral mixtures, and that it is the young leaves that are damaged. In the *peach*, alkaline washes are more injurious to youug than to old leaves, and neutral mixtures more injurions to old than young leaves. But, unlike the grape, the peach is sensitive to soluble copper and eventually the differences in behavior of the foliage following spraying are masked by copper injury. In the *tomato*, alkaline washes are more injurious than neutral Bordeaux mixtures, the injury due to alkalinity being noticeable on the young leaves. In the *apple*, neutral and alkaline Bordeaux mixtures of the usual types are injurious. The degree of alkalinity of the wash seems to have little or no influence on the intensity of the injury produced. However, the apple is somewhat sensitive to soluble copper and the fruit much more so than the foliage. In fact, the apple is so sensitive to soluble copper after the blossoms have fallen that Sanders and Brittain introduced Bordeaux mixtures in which the ratio of cupric sulfate to calcium oxide is 1:3 and 1:5 in order to reduce injury. Bordeaux mixtures of this type can be used on the apple very successfully, and cause very little if any injury. The reduction in the amount of the injury produced is not brought about, however, by any change in the nature of the copper precipitate formed, but by the fact that such a large excess of lime both delays and impedes carbonation and consequently the dissolution of the copper in meteoric water.

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Cellophane Plant under Construction

Cellophane, a transparent, cellulose product, used largely in millinery for decoration and in other trades for wrapping purposes, is to be manufactured by the du Pont Cellophane Co., a subsidiary of the E. I. du Pont de Nemours & Company. A plant to cost approximately $2,000,000 is now being constructed on the Niagara River at Buffalo, N. Y. This will be the first plant to manufacture this product in the United States. Cellophane has been produced in France for the past several years and its use is extending for wrapping purposes for confectionery, biscuits, cakes, tea, coffee, cocoa, meat products, and, in fact, for nearly all articles of food, as well as for perfumery, soap, various toilet preparations, pharmaceutical products, and others.

It is an important addition to the list of cellulose products produced by chemists for commercial uses during the last several years. It is nongelatinous, will not melt in boiling water, or decay. It is described as entirely harmless, water- and grease-proof, odorless, and can be dyed in any shade, printed or embossed, making it especially attractive as millinery decoration. It is manufactured in either sheets or rolls.

The du Pont Cellophane Company has obtained the patent rights for North America and pending the completion of its factory at Buffalo will be the selling agents in this country for the product. The company is now importing it. It is expected that the new factory will be completed in May or June of next year.

Analysis of Triphenylmethane and Azo Dyes by Titanous Chloride[1]

By W. S. Calcott and F. L. English

E. I. du Pont de Nemours & Co., Wilmington, Del.

The titanous chloride titration has been applied in the determination of strength of commercial dyes of the triphenylmethane and azo classes, satisfactory results having been obtained in the routine analysis of about thirty representatives of the former and over a hundred of the latter. The method gives results accurate to about 0.5 per cent.

ALTHOUGH the application of titanous chloride to the analysis of dyes was introduced by Knecht and Hibbert about twenty years ago,[2] little seems to have been done in the commercial application of the method, in this country at least, until the last few years. This seems to be attributable chiefly to the long-standing prejudice, on the part of both dye manufacturers and consumers, against any form of chemical analysis of dyes, upon the ground that the only criterion of the value of a dye is the dye test. While this is undoubtedly true so far as shade, fastness to light and washing, brightness, etc., are concerned, sufficient data are now available to prove the superiority of the chemical method in the estimation of strength. In the standardization of dyes for the trade, the titanous chloride titration has therefore supplemented rather than superseded the dye test.

Perhaps an even greater service is rendered as a guide and control in the manufacturing processes. The lack of a rapid and accurate method for determining the purity of dyes has been a source of embarrassment in the synthetic work in both laboratory and plant. Heretofore, the dye test has been the basis for the estimation of yields, but this method alone is unsatisfactory for the purpose, not only because of the large variations frequently encountered between duplicate determinations upon the same sample, but also because the results must be expressed in terms of some arbitrary standard, the composition of which is usually unknown. The results of the titanous chloride titration, on the other hand, may be calculated upon the basis of either absolute purity or the standard dye, as desired.

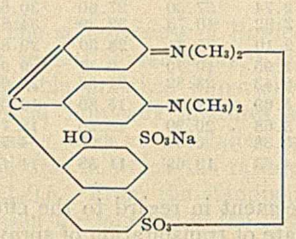
The determination of elemental constituents of the dye molecule, nitrogen, sulfur, etc., has been used to a slight extent, but little confidence can be placed in the results, since the impurities in the sample usually contain the element sought.

Preparation and Standardization of Solutions

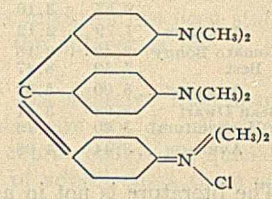
For all dye titrations a 0.05 *N* titanous chloride solution was used, the method of preparation, storage, and use having been previously described in detail.[3] Standardization was accomplished by means of Metanil Yellow purified as described later under the analysis of that compound. The procedure consisted in dissolving about 0.20 gram of the dye in 50 cc. of water and 50 cc. of 25 per cent sodium tartrate solution, boiling to expel air, and titrating the hot solution to a colorless end point in an atmosphere of carbon dioxide. Triplicate titrations should agree within 0.2 per cent in the normality factor.

Triphenylmethane Dyes

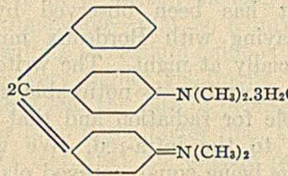
Three representatives of this class, Pontacyl Green S, Crystal Violet and Victoria Green, were studied, their titration presenting no difficulty.



Pontacyl Green S



Crystal Violet



Victoria Green

The reaction consists in the reduction of the dye to its leuco base with the consumption of two atoms of hydrogen, the analytical procedure being as follows:

> Dissolve the sample (equivalent to 30 to 50 cc. of 0.05 *N* titanous chloride) in a mixture of 50 cc. of water and 50 cc. of alcohol[4] in a 300-cc. Erlenmeyer flask. Add 50 cc. of 25 per cent sodium tartrate solution, boil 3 to 5 minutes, admit a rapid stream of carbon dioxide, and titrate the hot solution with 0.05 *N* titanous chloride to the last distinct color change, passing carbon dioxide throughout the titration. With average dye samples the end points are sharp, being determinable within two to four drops of titanous chloride.

The samples upon which the experimental work was done were purified by repeated crystallizations from water and alcohol, the purity of the final product being checked by nitrogen, sulfur, or chlorine determinations.

Wide variations were made in the conditions of the analysis, the results obtained upon Pontacyl Green S, set forth in the following tables, being typical of the other dyes studied and proving the titration to be independent of reasonable variations in procedure.

Table I—Effect of Concentration of Sodium Tartrate
(Assay = 0.3049 gram, 1 cc. $TiCl_3$ = 0.01219 gram dye)

No.	25% Sodium Tartrate Cc.	$TiCl_3$ Cc.	Purity %
1	5	No end point	...
2	10	About 25	...
3	18	24.05	96.20
4	20	24.08	96.32
5	25	24.05	96.20
6	50	24.10	96.40

In these experiments, one-half the proper size sample was used because of the small amount of purified material available. In Nos. 1 and 2, the color of the solution at the end

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[1] Presented before the Division of Dye Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] *Ber.*, **36**, 166, 1549 (1903); **38**, 3318 (1905); **40**, 3819 (1907); "New Reduction Methods in Volumetric Analysis," Longmans, Green & Co., **1910**, reprinted with additions in **1918**.

[3] This Journal, **12**, 994 (1920).

[4] Alcohol denatured with benzene is satisfactory.

of the titration was red and the end point indistinct. The fact that 18 cc. of the 25 per cent tartrate ($Na_2C_4H_4O_6.2H_2O$) are equivalent to the free hydrochloric acid in 25 cc. of the titanous chloride solution indicates that free mineral acid is detrimental, but in addition to this buffer action the tartrate has a specific effect since titrations in the presence of an equivalent amount of sodium acetate were unsuccessful.

TABLE II—EFFECT OF TEMPERATURE OF TITRATION
(Assay = 0.3049 gram, 1 cc. $TiCl_3$ = 0.01219 gram dye)

No.	Temp. ° C.	$TiCl_3$ Cc.	Purity %
1	50	24.06	96.24
2	60	24.03	96.12
3	70	24.07	96.28
4	Boiling	24.05	96.20

The temperature of titration is thus seen to have no appreciable effect upon the reaction.

TABLE III—EFFECT OF VARIATION IN ALCOHOL
(Assay = 0.3049 gram, 1 cc. $TiCl_3$ = 0.01219 gram dye)

No.	Alcohol Cc.	$TiCl_3$ Cc.	Purity %
1	..	23.81	95.24
2	15	23.93	95.72
3	25	24.12	96.48
4	50	24.10	96.40

In Nos. 1 and 2 the sample was not in complete solution. The concordant results of Nos. 3 and 4 indicate that alcohol, in excess of a certain necessary minimum, has no effect.

The following analyses were made upon material that had been crystallized three times:

TABLE IV—ANALYSIS OF PURE PONTACYL GREEN S
(Assay = 0.6097 gram, 1 cc. $TiCl_3$ = 0.01219 gram dye)

No.	$TiCl_3$ Cc.	Purity %
1	49.85	99.70
2	49.92	99.84
3	49.89	99.78
4	49.97	99.94
5	50.03	100.06
6	49.90	99.80
	Average	99.85

Crystal Violet behaved in all respects like Pontacyl Green S, but in the analysis of Victoria Green a little difficulty was encountered due to the variable composition of the dye samples. The formula for this dye given in the standard reference books shows the commercial article to contain two mols of dye base to three of oxalic acid, which would give an oxalic acid content of 29.1 per cent. When, however, pure material was prepared by repeatedly recrystallizing from 1 per cent aqueous oxalic acid solution and drying to constant weight *in vacuo* at 40° C., the product, when analyzed by the procedure found satisfactory for Pontacyl Green S, gave results varying from 103.2 to 104.4 per cent, calculated on the basis of the preceding formula. These high results cast suspicion upon the oxalic acid content, to confirm which oxalic acid determinations were made through the gravimetric calcium oxalate procedure. These showed the oxalic content of different samples to be quite variable, results between 23.0 and 26.3 per cent oxalic acid being obtained; the lower values were yielded by the samples crystallized from water and the higher by those from dilute oxalic acid. When this indefiniteness of constitution was taken into consideration, satisfactory analyses were obtained by the titration method, as indicated by the results set forth below, obtained upon samples crystallized from dilute oxalic acid.

TABLE V—COMPLETE ANALYSIS OF VICTORIA GREEN SAMPLES

CONSTITUENT DETERMINED	Sample A %	Sample B %
Dye by $TiCl_3$ (calcd. without $H_2C_2O_4$).......	72.40	72.58
$H_2C_2O_4$...........................	26.14	26.30
H_2O (50° C., *in vacuo*)....................	1.12	1.27
TOTAL..............................	99.66	100.15

In addition to these three dyes studied in detail, the titration has been applied successfully in the routine laboratories to various other triphenylmethane colors.

AZO DYES

In attempting to apply the methods for the titration of azo dyes recommended by Knecht and Hibbert,[5] difficulty was frequently encountered in the high color of the reduced solution, which masked the end point of the titration. Investigation revealed the fact that this color depends to a large extent upon the nature of the medium in which the sample is dissolved, so that by a judicious choice of solvents the direct titration of a dye is made possible which otherwise would require the less convenient indirect method. Unfortunately, no means of predicting the required solvent mixture from the constitution of the sample has been established to date; consequently, in undertaking the analysis of a new dye, the medium must be determined by trial. On the other hand, the data acquired in the analysis of a large number of azo dyes show that any combination of the solvents experimented with which yields a sharp end point gives concordant results of sufficient accuracy for commercial purposes. It may also be stated that in all direct titrations of azo dyes the presence of sodium tartrate (or Rochelle Salt) is either absolutely necessary or highly advantageous and, conversely, in all back titrations excess of sodium tartrate must not be present since titanous chloride is decomposed upon boiling in the absence of free mineral acid.

From these considerations it is evident that no procedure of universal application can be given. The general outline of the methods employed is as follows:

DIRECT TITRATION—Dissolve the sample, which should be equivalent to 30 to 50 cc. of 0.05 *N* titanous chloride, in 50 to 100 cc. of an appropriate solvent (water, alcohol, acetic acid, or mixtures of these) in a 300-cc. Erlenmeyer flask, add 50 cc. of 25 per cent sodium tartrate solution, and boil for 3 to 5 minutes. Admit a rapid stream of carbon dioxide, connect the flask to the buret, and titrate the hot solution with 0.05 *N* titanous chloride to the last distinct color change. If the standard solution is added in 0.2-cc. portions toward the end of the titration, a satisfactory end point can be detected in even a quite highly colored solution.

INDIRECT TITRATION—Dissolve the sample (equivalent to about 30 cc. of titanous chloride solution) in 50 to 100 cc. of solvent, add 25 cc. of 40 per cent sulfuric acid or concentrated hydrochloric acid, boil to expel dissolved air, sweep with carbon dioxide, and add 50 cc. of 0.05 *N* titanous chloride solution. Boil 5 minutes and titrate the hot solution with 0.05 *N* ferric alum solution. It frequently happens that the reduction products of the dye serve as indicator, but if this is not the case 2 cc. of a 0.1 per cent solution of reduced Methylene Blue should be added previous to the back-titration. This indicator is prepared by dissolving 0.5 gram of dye in 100 cc. of 50 per cent alcohol and 50 cc. of 25 per cent sodium tartrate solution, titrating hot with titanous chloride to discharge off the blue color and diluting to 500 cc. The solution should be stored under carbon dioxide, as it is rapidly reoxidized by air.

Either method is rapid, the direct titration requiring 15 to 20 minutes and the back titration but little longer, and the results by either, when applied to average samples, should be reproducible within about 0.5 per cent. In the analysis of dye mixtures, the results cannot be calculated upon the absolute basis of the Metanil Yellow standardization, but must be expressed in terms of a standard dye known to contain the same ingredients as the sample in approximately the same ratio.

In all cases the samples dealt with were purified by recrystallization from water or mixtures of alcohol and water, and the purity of the final product was checked by elementary analysis. Since Metanil Yellow was used as the ultimate standard, especial care was exercised in its purification,

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[5] "New Reduction Methods in Volumetric Analysis," 1918, p. 76.

TABLE VI—ANALYSIS OF AZO DYES BY TITANOUS CHLORIDE

DYE	Molecular Weight	COMPOSITION	Procedure	Normality of $TiCl_3$	Assay G.	Solvent Cc.	$TiCl_3$ Cc.	Iron Cc.	Purity by $TiCl_3$ %	Purity by Sulfur or Nitrogen %
Metanil Yellow	375.3	Metanilic acid + diphenylamine	..	.....	0.2000	....	46.85	...	100.04	......
			1	0.04897	0.2100	50 water	49.15	...	99.96	N, 99.8
			..	.....	0.2299	....	50.01	...	100.02	......
Orange II	350.2	Metanilic acid + ρ-naphthol	..	.....	0.2000	....	49.96	...	99.56	......
			1	0.04552	0.2000	50 water	50.06	...	99.76	......
Chrome Black 6B	394.3	1:2:4 acid + ρ-naphthol	..	.....	0.2415	50 alcohol	49.50	...	99.00	......
			1	0.04897	0.2415	25 water	49.50	...	99.00	N, 98.5
			..	.....	0.2415	25 acetic	49.40	...	98.80	S, 99.3
Sky Blue 6B	992.7	Dianisidine + 2 Chicago acids	..	.....	0.2824	....	44.25	...	88.50	......
			1	0.04552	0.2824	50 water	44.45	...	88.90	N, 88.5
			..	.....	0.2824	50 alcohol	44.40	...	88.80	S, 88.6
Basic Brown G	419.2	3-Phenylenediamine	..	.....	0.1259	....	50.00	12.20[a]	74.00	......
			2	0.04803	0.1259	100 water	50.00	12.20	74.00	N, 74.5
			..	.....	0.1259	....	50.00	12.00	74.40	......
Basic Brown B	461.3	3-Tolylenediamine	..	.....	0.1388	....	50.00	5.40[a]	87.40	......
			2	0.04803	0.1388	100 water	55.00	9.90	87.00	N, 87.6
			..	.....	0.1388	....	60.00	14.60	87.00	......
Chrysoidine R	262.7	Tolylenediamine + aniline	..	.....	0.1577	....	49.90	...	99.80	......
			1	0.04803	0.1577	50 water	49.85	...	99.70	N, 99.05
			..	.....	0.1577	25 acetic	49.92	...	99.84	......

[a] 1 cc. of iron solution = 1.062 cc. of $TiCl_3$.

the crystallizations—two from water and three from alcohol—being continued until the final crop of crystals and the material obtained upon concentration of the last mother liquor consumed identical percentage quantities of titanous chloride. The final product was dried to constant weight at 120° C.

In the foregoing table are summarized typical results obtained upon representative azo colors. In Column 4, the figures 1 and 2 refer, respectively, to the direct and indirect titration procedures.

BASIC BROWNS AND CHRYSOIDINES

In the analysis of the Basic Browns and Chrysoidines, a special procedure is necessitated by the instability of these compounds toward heat. In the former case, which is an indirect titration, the sample was dissolved, the flask swept with carbon dioxide, and the titanous chloride added at room temperature, after which the reaction mixture was boiled and the determination completed according to the usual procedure. With the Chrysoidines, titration was begun at 65° C., temperatures above 70° C. causing appreciable decomposition with consequent low results.

ADDITIONAL WORK

In addition to the dyes studied above in detail, the titration method has been successfully applied in the routine laboratories to the analysis of about twenty-five triphenylmethane and over a hundred azo colors.

Since the completion of this investigation, the titration of azo dyes with titanous chloride with electrometric determination of the end point has been described by Jones and Lee.[6] It is probable that such a procedure would overcome, to a considerable extent at least, the arbitrary effect of solvent upon the titration encountered in our work.

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[6] THIS JOURNAL, 14, 46 (1922).

Action of Barium Chloride on Sulfate in Fused Salts[1]

By Howard E. Batsford

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The action of barium chloride on sulfate in aqueous solution is so well known as not to need repetition, but whether this same action took place when in a mixture of fused salts, such as sodium and calcium chlorides, was an open question. Foote and Martin,[2] as a result of investigations on the action of barium chloride in fused mercuric chloride, found that the chlorides of most of the divalent metals were not soluble in mercuric chloride. However, this work, though of a similar nature to that undertaken by the writer, was not conclusive evidence that the reaction $BaCl_2 + R_2SO_4 = BaSO_4 + 2RCl$ would occur in quantitative amount in other fused salts.

In connection with the electrolysis of fused salts it is very desirable to obtain as pure salt as possible, in order to prevent irregularities in the electrolytic action. The usual practice is to purify the salts in aqueous solution, then to dehydrate them thoroughly and proceed to fuse them for manufacture of the respective metals.

An effort was made to study the effect on electrolysis of adding slightly impure or commercial salts to the fused cell. The result was a lowering of the current yield coupled with foaming of the bath and disturbed thermal relations. It was found that barium chloride added from time to time had an accelerating action on the metal production, but to what this action was attributable was unknown. The questions naturally arose, whether barium chloride affected the cell by reaction with the sulfate impurities, and what effect it had on the fusion point when added in small quantities to the melt.

The second question was settled definitely in a short time by making up known mixtures of sodium and calcium chloride, analyzing them, and running them for freezing points, then repeating the operation with samples containing varying small quantities of the barium salt (Fig. 1).

The experiment on the action of barium chloride on the sulfate occupied several days. During the regular operation of the electrolytic cell barium chloride was added hourly in known amounts, samples of the molten electrolyte and bottom sludge being taken at proper intervals.

Analyses were made of all materials entering and leaving the furnace, as well as of the material remaining at the end of the run. On account of the length of each run and the large quantities of electrolyte employed, the chance of large percentage loss was remote.

It was found that (1) barium chloride did not change the freezing point when added in small quantities; (2) barium chloride in molten salt mixtures acted as a purgative, precipitating quantitatively the sulfate existing as impurity in the salts.

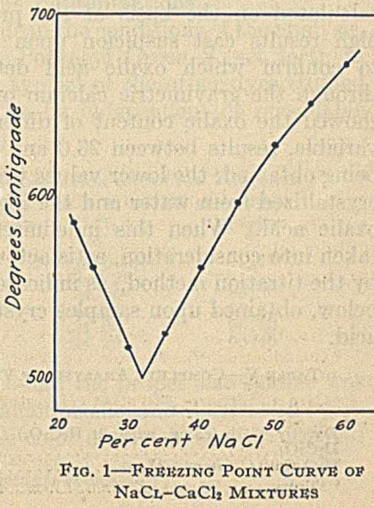

FIG. 1—FREEZING POINT CURVE OF NaCl–$CaCl_2$ MIXTURES

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[1] Received May 21, 1923.

[2] *Am. Chem. J.*, 41, 451 (1909).

A Method for the Determination of Tolidine[1,2]

By S. Palkin

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THE determination of tolidine by nitrite titration[3] has an apparent advantage in that it is comparable to the process involved when the base is to be used for tetrazo dyes. This method is, however, subject to the usual difficulties incident to diazotization, such as uncertainty of end point with starch iodide indicator, as well as instability of the product formed. The reaction is, moreover, a time reaction, requiring periodic standing and observations, to approximate completion of the diazotization. An iodometric method[4] described by Roesler and Glasmann has similar disadvantages and depends upon spot tests for determination of the end point. Both methods, while simple, require considerable skill and practice before any degree of accuracy can be approximated.

It is well known that tolidine and benzidine form a number of very difficultly soluble salts, and advantage has been taken by Raschig[5] and others[6] to make use of the sulfates of these bases for determination of the sulfate radical. No method which makes use of this property of tolidine for the determination of the base itself, however, has been found on record. The Raschig[5] method requires an excess of tolidine to insure complete precipitation.

The method described in this paper makes use of the more soluble salt, the dihydrochloride of tolidine, and depends upon the fact that the dihydrochloride can be removed from aqueous solution by the introduction of saturated salt solution. The tolidine dihydrochloride, which is freed from excess hydrochloric acid and other impurities by washing with salt solution, can then be titrated acidimetrically, using a suitable indicator.

DESCRIPTION OF METHOD

About 0.5 to 1 gram of sample is dissolved in dilute, 1 *N* hydrochloric acid solution, using heat. About 10 cc. of 3.5 per cent acid will be required per gram of tolidine. To the tolidine solution is then added a saturated sodium chloride solution, using about 100 cc. of saturated salt solution to every 10 cc. of tolidine solution. The tolidine dihydrochloride is allowed to crystallize out for about 20 or 30 minutes and is filtered by suction through a small 3 or 4-cm. paper on a perforated plate. The precipitate is washed several times with saturated salt solution to remove all free acid and other impurities.

The precipitate of tolidine dihydrochloride is then transferred completely to a 150-cc. beaker, paper and all, and dissolved in hot water to a clear solution. To this solution is added 0.1 *N* ammonium hydroxide solution slightly in excess, as determined by methyl red indicator. About 55 cc. of 0.1 *N* ammonium hydroxide per 0.5 gram of tolidine is a convenient amount. The precipitate of tolidine base is then allowed to stand a few minutes, filtered by suction, and washed with water. The excess ammonia is titrated back with 0.1 *N* hydrochloric acid solution, using methyl red as indicator, and the volume of ammonium hydroxide consumed is obtained by difference. One cubic centimeter of 0.1 *N* ammonium hydroxide equals 0.0106 gram of tolidine. Standard sodium or potassium hydroxide may be used instead of ammonia, but the usual precaution to keep it free from carbonate must be taken.

Using this method in a series of tests on specially purified tolidine with melting point 129° C., it was possible to account for 99.82 per cent in an average of nine determinations. The minimum recovery in these experiments was 99.52 per cent, and the maximum recovery was 99.96 per cent. The recovery on a less pure sample of tolidine with melting point of about 128° C. showed variations of the same magnitude. These results are shown in Table I.

TABLE I—APPLICATION OF METHOD

No.	Tolidine Taken Grams	Standard Alkali Consumed Cc.	Tolidine Found	
			Grams	Per cent
1[a]	0.2500	22.95	0.2494	99.76
2	0.2500	22.95	0.2494	99.76
3	0.2500	22.9	0.2488	99.52
4	0.5000	46.0	0.4998	99.96
5	0.2500	23.0	0.2499	99.96
6	1.0000	91.9	0.9985	99.85
7	0.5000	45.9	0.4987	99.74
8	0.5000	45.95	0.4993	99.86
9	0.2500	23.0	0.2499	99.96
11[b]	1.0000	91.5	0.9941	99.41
12	0.7500	68.5	0.7443	99.2
13	0.1000	9.1	0.0989	98.9
14	0.0500	4.7	0.0510	102.0
15	1.0000	91.5	0.9941	99.41
16	1.0000	91.5	0.9941	99.41
17	0.5000	45.8	0.4976	99.52
18	0.2500	22.8	0.2477	99.08
19	0.1000	9.1	0.09887	99.87
20	0.0500	4.55	0.0494	98.86

[a] Nos. 1 to 9 obtained by further purification from *b*, melting point 129° C.

[b] Nos. 11 to 20 obtained by purification of technical tolidine.

Experiments were also conducted to determine whether the method was sensitive to variations in salt and acid concentrations. As shown in Table II, these two factors are without appreciable effect.

TABLE II—EFFECT OF VARIATIONS IN HYDROCHLORIC ACID AND SODIUM CHLORIDE CONCENTRATIONS

No.	Tolidine Solution[a] Cc.	Salt Solution Used Cc.	HCl Added Cc.	Standard Alkali[b] Consumed Cc.	Tolidine Found Grams
21	5	50	...	22.6	0.2455
22	5	50	...	22.5	0.2445
23	5	50	0.1	22.5	0.2445
24	5	50	0.2	22.5	0.2445
25	5	50	0.5	22.6	0.2455
26	5	50	1.0	22.45	0.2439
27	5	50	2.0	22.8	0.2477
28	5	50	3.0	22.55	0.2450
29	5	50	4.0	22.6	0.2455
30	5	50	5.0	22.65	0.2461
31	5	50	...	22.5	0.2445
32	5	50	...	22.8	0.2477
33	5	50	...	22.55	0.2450
34	5	50	...	22.65	0.2460
35	5	40	...	22.45	0.2439
36	5	40	...	22.45	0.2439
37	10	90	...	45.1	0.4900
38	10	100	...	45.2	0.4911
39	10	80	...	45.2	0.4911
40	10	100	...	45.3	0.4921

[a] Approximately 10 grams tolidine and 12 cc. concentrated hydrochloric acid dissolved in 200 cc. water. 1 cc. contains approximately 50 mg. tolidine.

[b] NH_4OH solution used was 0.10245 *N*.

NOTE: Probable error in pipetting tolidine solution = 1 drop (0.05 cc.) which is 50 × 0.05 = 2.5 mg.

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[1] Presented before the Division of Dye Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] Contribution No. 78 from the Color Laboratory, Bureau of Chemistry, Washington, D. C.

[3] Cain and Thorpe, "Synthetic Dyestuffs and Intermediate Products," **1918**, p. 312.

[4] *Chem. Ztg.*, **27**, 986 (1903).

[5] *Z. angew. Chem.*, **26**, 617 (1903).

[6] Müller and Dürkes, *Z. anal. Chem.*, **47**, 477, 653 (1903).

Some Simplified Routine Tests in Sugar-Mill Laboratories[1]

By K. R. Lindfors

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Every beet-sugarhouse chemist is familiar with the apparently endless stream of samples brought into the laboratory to be tested, also with the fact that the work must be performed to a great extent by benchmen with often no knowledge of analytical chemistry. Such conditions undoubtedly exist in the great majority of sugar mills, and in order to accomplish the work only methods of greatest speed and simplicity can be utilized. Therefore, modifications increasing the speed, or decreasing the chance of error, ought to be of interest to sugarhouse chemists.

The purpose of this paper is to call attention to a few simplified methods, little known, or such modifications thereof as have been found necessary in order to insure reliable results or lessen the work involved.

Determination of Sugar in Lime Cake

THE official method of decomposing the saccharate of lime present with acetic acid requires considerable time as the acid should be added very slowly in order to insure complete decomposition without excess. A modification involving the addition of a definite amount of acetic acid is sometimes used, but as the composition of the lime cake varies considerably from time to time, this amount may be either too large or too small. Ammonium nitrate has been substituted in many cases, but it is not only expensive, but rapidly corrodes the brass fittings on the polariscope tube.

Herles[2] recommends the use of ordinary neutral lead acetate for decomposition of the saccharate present. The lead acetate combines with the lime producing calcium acetate and hydroxide of lead, setting the sugar free.

As 2 molecules of lead acetate combine with 1 molecule of calcium oxide, 1 gram of lime will require 13.54 grams of lead acetate. Lime cake ordinarily does not contain more than 4 per cent of caustic lime; 14.11 grams of the reagent will therefore be sufficient for normal weight of the cake.

Furthermore, as about 5 cc. of insoluble matter are present in 26 grams of cake, it becomes necessary to fill up to 105 cc. in order to get a direct percentage of sugar. Hence, the total volume to be added is 86.98 cc. which must contain 16.22 grams of the acetate. But as an excess does no harm, it is recommended to use 20 grams of lead acetate per 100 cc. of water. The advantage of this reagent lies in the fact that it not only decomposes the saccharate present, but at the same time precipitates the impurities, as the hydroxide formed during decomposition combines with the excess of the reagent to basic acetate of lead.

Usually, there are no 105-cc. flasks available. Herles, therefore, recommends the following modification of his method:

> Weigh out 30 grams of lime cake, add with a pipet 100 cc. of the lead acetate solution, mix, filter, and polarize. If the weighing is done in a dish with a tight fitting cover in which is placed a piece of a suitable brass chain, a few moments of violent shaking will accomplish the mixing of the reagent and the lime cake.

The method gives very good results in straight sugar mills, but when the Steffen process is used the amount of caustic lime present is sometimes considerably greater; therefore, the amount of lead acetate added according to the foregoing directions is not sufficient to complete the decomposition of the saccharates. The difficulty was finally overcome by the use of 25 grams of lead acetate per 100 cc. (in place of 20 grams) and the addition of 1 to 2 cc. of concentrated or glacial acetic acid per liter, the amount of acetic acid to be added depending upon the presence of carbonate of lead in the commercial product. In straight houses sufficient acetic acid to insure a perfectly clear solution was used, and in Steffen's, 1 to 2 cc. additional.

Steffen's Waste and Wash Waters—As neutral or slightly acidulated lead acetate so effectively broke up the saccharate present in lime cake, its use for similar purpose in other materials containing bound sugar was naturally suggested. It was therefore tried in place of acetic acid on Steffen's waste and wash waters. The result was very satisfactory. A large number of experiments were made, with good checks, and finally this procedure was adopted:

> With a sucrose pipet transfer double normal weight of Steffen's waste or wash waters into a 100-cc. flask. Add two drops of phenolphthalein, and add slowly, under constant shaking, a concentrated solution of slightly acidulated lead acetate (about 450 grains lead acetate, and 2 cc. acetic acid per liter) until the red color disappears. Then add about 2 cc. more or sufficient to break up the milky precipitate, fill up to mark, filter, and polarize.

Saccharate Cake and Solution from Cooler—These materials contain too much caustic lime to be completely decomposed by acetate of lead, but by ending the reaction with this solution the danger of an excess of acetic acid is avoided, and no further clarification is required. The method adopted is as follows:

> To normal weight of the material add dilute acetic acid until the red color imparted by two drops phenolphthalein disappears for the first time. The red color soon returns upon further shaking, and then complete the decomposition by an excess of concentrated neutral lead acetate. (About 450 parts of lead acetate to 1 liter of water, plus 1 cc. concentrated acetic acid.)

Determination of Sucrose and Raffinose in Molasses

The old Herzfeld method works well with ordinary sugarhouse products, but when Steffen house molasses has to be analyzed the results are often far from satisfactory. The reason therefore is not hard to find. This molasses contains such large amounts of the salts of lime, potash, and soda, mostly as carbonates, that a part of the hydrochloric acid is neutralized thereby and therefore the inversion is not completed in the time specified. To try to overcome this difficulty by an addition of more acid or longer heating is not advisable, as the composition of the molasses is not constant. Therefore, a considerable error would be introduced when such a modification was used on molasses with less salts, and often the chemist does not know what kind of molasses he is testing, nor is he able to estimate the amount of carbonates present.

Walker[3] describes an inversion process for the determination of sucrose by double polarization, which apparently showed a way out of the difficulties. His method for determination of sucrose in cane-sugar molasses is briefly as follows:

> Place 50 or 75 cc. of the solution used for direct polarization in a 100-cc. flask (in case 50 cc. are used add 25 cc. water) and heat in a water bath to 65° C. Remove from bath, add 10 cc. of a

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[1] Presented before the Division of Sugar Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] *Z. Zuckerind. Landw.*, 727 (1898).

[3] This Journal, **9**, 490 (1917).

mixture of equal volumes of hydrochloric acid (sp. gr. 1.188) and water, allow to cool down spontaneously in air for 15 minutes, or as much longer as may be convenient, then cool in water to room temperature, make up to 100 cc., and polarize as usual. In the case of low-grade products which have been clarified with a large excess of basic lead acetate, it is imperative that the excess alkalinity be neutralized before heating, this being best accomplished by the addition of 1 cc. (or 2 cc. in exceptional cases where a large excess of dry lead acetate has been used) of the dilute acid used for inversion.

When this method was applied to Steffen house molasses, it was found that the inversion was not completed within the time mentioned, more acid, longer time, or both, evidently being required. After a considerable amount of experimental work the method was finally adopted with the following modifications:

(1) The hydrochloric acid used is prepared by adding 40 cc. of water to 60 cc. of concentrated acid, in place of 50: 50 in the original method.

(2) One cubic centimeter of this acid is always added before heating.

(3) The contents of the flask is heated to 70° C. on the water bath (in place of 65° C.).

(4) The time of inversion before cooling is increased to 45 minutes.

(5) The chloride of lead precipitated is removed by filtration before the zinc dust is added.

Thus, the procedure is carried out in this manner:

Weigh out double normal weight of the molasses and transfer to a 200-cc. flask with water. Add basic lead acetate until no more precipitate is formed (25 cc. will generally be about right), fill up to mark, mix well, filter, and polarize in a 100-mm. tube. The reading multiplied by 2 gives direct polarization. Pipet 50 cc. of the filtrate to a 100-cc. flask, add 25 cc. water and 1 cc. hydrochloric acid (40 cc. water to 60 cc. concentrated hydrochloric acid). Insert a thermometer in the flask, and heat the contents on a water bath to 70° C. Remove the flask from the water bath and introduce 10 cc. of the dilute hydrochloric acid. Let stand in the air at room temperature for at least 45 minutes, cool, fill up to mark, and filter. Add a knife point of zinc dust, filter the solution and polarize again.

DETERMINATION OF MOISTURE IN DRIED PULP

Although it is of great importance to keep the moisture of dried pulp as constant as possible within narrow limits, the control thereof by the laboratory has been very unsatisfactory on account of the long time required for drying, even when vacuum ovens are available. In some plants the drying time has been cut down to one hour, and the moisture calculated by means of a factor in order to obtain at least an approximate result rapidly. But even so, a large amount of pulp has time to pass through the drier before the results are known. Therefore, a method of shortening the time of the determination, and at the same time giving the moisture accurately, ought to be of great value for the control of the drier work. The moisture tester[4] is an apparatus for distilling off the water contained in the sample, and is especially, and hitherto probably exclusively, used for the determination of moisture in grain. The grain is immersed in oil and heated to a specified temperature (in most cases to 190° C.) at which all the water distils off, to be collected in a cylinder so graduated that the reading of the liquid gives the percentage of moisture in the sample. As 50 or 100 grams of material are taken, the moisture present can be determined within 0.1 to 0.05 per cent.

As no information was available as to the procedure to be followed for determination of moisture in pulp, it became necessary to ascertain experimentally the amount of material to be taken, the volume of oil, and the temperature. Time did not permit a thorough investigation of all details, but the results obtained with the following method checked very well with the percentage of moisture found after 12 hours of drying at 105° C. in an ordinary drying oven.

Weigh out 50 grams of the pulp and transfer to distilling flask. Add 250 cc. of oil, and heat until the thermometer registers 190° C.

The whole operation is finished in 20 minutes. The apparatus is inexpensive and the oil can be used over and over again. This apparatus ought to be found in every sugarhouse laboratory.

Some experiments were also made to find out if the apparatus could be used for the determination of water in other sugarhouse products. With pressed pulp no satisfactory results were obtained, as the large amount of water present (about 85 per cent) caused excessive foaming. This can, of course, be overcome by the use of small amounts of sample, but then the accuracy of the method will be greatly decreased.

Water in molasses, fillmass, and sugar can be found by this method. Use 50 grams of material, 150 cc. of oil, and heat slowly to 170° C. However, variations of the materials may make modifications in the amounts necessary, and so far not enough experimental work has been done to ascertain the influence thereof.

DETERMINATION OF GUMS IN DIFFUSION JUICE

Where the apparatus for determination of potash by means of the centrifugal method is available, it will probably be of interest to know that the same can also be used for the determination of gums in diffusion juice.

To 5 cc. of diffusion juice add 0.5 cc. concentrated hydrochloric acid, and 15 cc. of 95 per cent (volume) alcohol. Mix well and let stand in water of about 70° C. for 15 minutes. Mix, transfer to a potash flask, and spin in motor-driven centrifugal for 15 minutes. Each degree on stem corresponds to 0.04 per cent of gums.

The absolute percentages obtained in this manner may not always be correct, but the figures are of considerable comparative value, since they indicate irregularities in the battery work, decomposed beets, and in a general way aid in comparing the beets of one plant with those of another.

The test is always run in duplicate (this is necessary to balance the centrifugal) and the mean of the two readings is taken.

PREPARATION OF STANDARD ACID

Many years ago the "Vereinslaboratory" in Berlin worked out the use of borax as a standard of preparation of normal solutions. As this salt furnishes an excellent check for such solutions, it is surprising that it is never mentioned in the chemical handbooks. The reason may be that borax loses some of its crystal water quite rapidly, but as the recrystallization thereof is very simple and rapid, this does not prevent its use. In the hands of men with little analytical experience or scientific education, it is probably the most accurate check available.

Commercial borax is recrystallized twice, C. P. borax once, preferably by letting the hot, concentrated solution (100 grams to 100 cc.) drop through a filter paper in a dish placed in cold water, under constant stirring. It is absolutely necessary to have the crystals form rapidly, under constant stirring, as large crystals are liable to enclose particles of the mother liquor. The fine crystals are washed once or twice with cold water, and the excess of water is removed by suction. Part of the moisture remaining is eliminated by pressing the crystals between filter papers until the papers no longer show any indication of moisture. The crystals are left to

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[4] For complete description of the apparatus and directions for its use see *U. S. Dept. Agr., Bur. Plant Industry, Circ.* **72**.

dry in the air, at room temperature, for 24 to 72 hours, depending upon the moisture in the air of the room. In winter, if no steam vapor is present, 24 hours are generally sufficient. No heating or drying in desiccators is permitted, as then some of the crystal water is lost.

The high molecular weight of this salt will practically eliminate the effect of errors due to slight inaccuracy in weighing, or small impurities still present. Five grams of borax correspond to 26.2 cc. of normal acid; 19,109 grams to 1/10 normal, and 6.825 grams to 1/28 normal acid.

Methyl orange is generally recommended as an indicator for borax solution, but it is somewhat lacking in sharpness, especially in dilute solution. This difficulty has now been overcome by the use of dimethylamidoazobenzene. This indicator is prepared by dissolving 1 gram of the salt in 1 liter of alcohol. The end point is very sharp.

High-Speed Stirring as an Aid to Chemical Action[1]

By C. H. Milligan and E. Emmet Reid

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The relation of speed of stirring to velocity of reaction has been studied in the ethylation of benzene and in the hydrogenation of cottonseed oil in presence of nickel. In both cases the reaction rates are nearly proportional to speed of stirring.

CONTACT is conceded to be essential to chemical action, and it is usual to shake or stir mixtures to facilitate reactions, but quantitative data connecting the violence of the agitation with the rates of reactions are lacking. Such data are desirable for the design of equipment. Of course, conclusions drawn from small-scale laboratory experiments are not to be applied recklessly to plant apparatus.

Where we have two consecutive reactions, one of which is extremely rapid and the other slow, the over-all velocity depends on the slow reaction and is related to the circumstances that favor or hinder it. If we consider the mutual solution of the reactants as the first of the two reactions followed by a chemical change, we come to the conclusion that if the desired reaction is rapid but the rate of solution is slow, the reaction rate will be related to the rate of stirring, while if the solubility is great and the reaction comparatively slow, stirring will be of little importance. The present investigation is a preliminary study of the relation between speed of stirring and reaction rate in several nonhomogeneous systems.

In the action of sulfur dioxide on benzene in the presence of aluminium chloride, stirring has little influence, since the gas dissolves readily anyway and the reaction rate is probably slow, but the absorption of ethylene by benzene in presence of aluminium chloride and the hydrogenation of cottonseed oil using nickel as catalyst are enormously accelerated by intensive stirring.

With the apparatus used by the authors and over the range covered by their experiments, the rates of these two reactions are roughly linear functions of the speed of stirring, and may be approximately expressed by $v = a + br$, in which v is rate of gas absorption and r is speed of stirring. The rate when the gas is only bubbled through is a, and b is a constant for a particular stirrer.

In the ethylation of benzene, a has a considerable positive value since the gas is moderately soluble in the liquid, while in the hydrogenation experiments a is negligible. Here the absorption of hydrogen increases faster than the rate of stirring for low speeds, the relation becoming linear at higher speeds. In Fig. 1 the absorptions in cubic centimeters per minute are plotted against speeds of stirring in thousands of revolutions per minute.

At 13,000 r. p. m. 1 volume of benzene was reacting with 6.5 volumes of ethylene, and 1 volume of cottonseed oil in presence of 0.12 per cent nickel was taking up 2.3 volumes of hydrogen, whereby its iodine number was being lowered 2.6 per minute.

For the literature relative to the ethylation of benzene by ethylene and for details as to the products obtained, reference may be made to a previous article.[2]

Rapid stirring appears to aid the chlorination of toluene and of acetic acid, but quantitative comparisons have not been made.

The Stirrer (Fig. 2)

The speed of the motor was 1700 r. p. m., which was multiplied about eight times by an arrangement of pulleys carried on a steel frame. Ball bearings were provided for the stirrer shaft and for the upper end of the countershaft. The speed of the motor was controlled by a variable resistance. The speed of the stirrer was measured by a speed counter, the end of which carried a toothed wheel which meshed with a thread

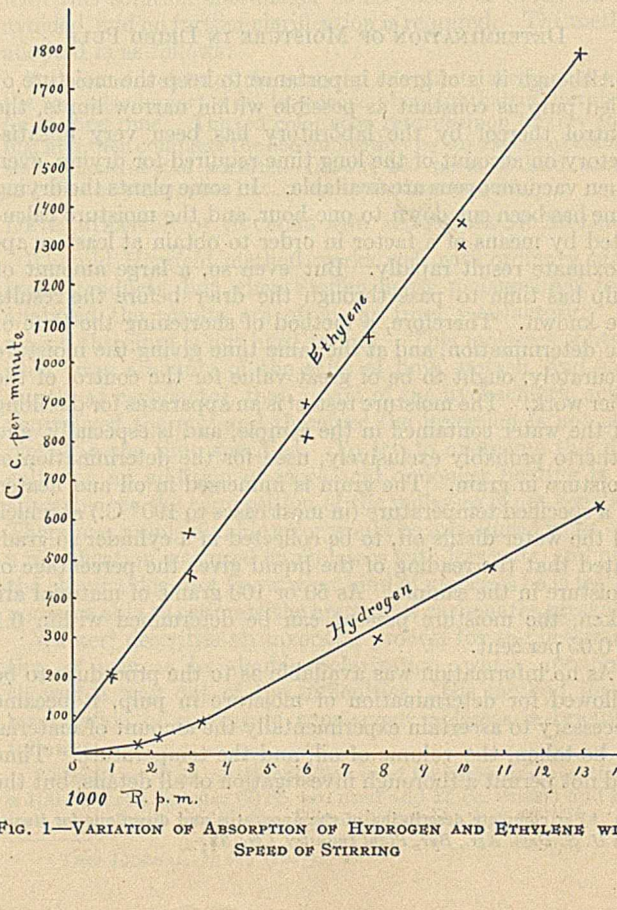

Fig. 1—Variation of Absorption of Hydrogen and Ethylene with Speed of Stirring

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[1] Received May 10, 1923.

[2] *J. Am. Chem. Soc.*, **44**, 206 (1922).

cut in the top end of the stirrer shaft. The speed counter was mounted on a swivel joint so that it could be snapped in and out of gear in taking the readings.

The reaction vessel was a glass bottle which was heated in a water or oil bath. The stirrer head was a disk, 37 mm. in diameter, carrying a bell-shaped projection at the bottom. Into the central cavity were drilled eight 2-mm. radial holes. The delivery tube for the gas terminated just beneath the bell. The stirrer shaft was surrounded by a tube which was carried by the frame above and passed tightly through the stopper, thus making a liquid seal for the stirrer shaft. To prevent swirling of the liquid large baffles were provided. These were carried by round rods passing through the stopper. By means of pliers applied to the projecting squared upper ends of these rods the baffles could be turned in so as to pass through the neck of the bottle.

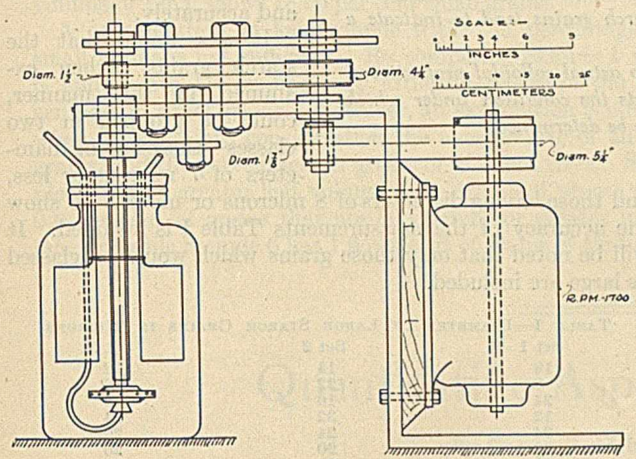

Fig. 2—The Stirrer

Experimental

Ethylation of Benzene—A mixture of 250 grams of benzene and 50 grams of anhydrous aluminium chloride was kept at 80° C. and ethylene passed in, the speed of the stirrer being adjusted so that only an occasional bubble of gas escaped absorption. The rates of stirring and of gas flow were read and then the gas rate was changed. In a run in which constant conditions of stirring, etc., are maintained, the reaction velocity increases for a time and then remains fairly constant for a considerable period, changing gradually as the ethylation proceeds. The measurements made here were all from a single run. Sufficient time was allowed for the reaction to get well under way before starting readings and then the adjustments were made as quickly as possible and the readings taken with the passage of a minimum amount of gas so as to avoid great changes in the composition of the mixture. To produce monoethylbenzene 77 liters of ethylene would have been required, which is several times the volume necessary for the readings. The ethylene was passed through a meter and the time given is for 0.01 cubic foot or 283 cc. The results are given in Table I, the last column of which shows the roughly constant values of *b*.

Table I—Absorption of Ethylene

R. p. M.	Seconds per 283 Cc.	Cc. per Minute	Increase Due to Stirring	*b*
0	..	80	...	...
1000	84	202	122	122
1000	87	196	116	116
3000	30	565	485	162
3000	37	457	377	126
6000	19	896	816	136
6000	21	810	730	122
7600	16	1065	985	129
8000	15	1135	1055	132
10,000	12.5	1360	1260	126
10,000	13	1300	1220	122
13,000	9.5	1790	1720	132

Hydrogenation—As the rate of hydrogenation varies with the proportion absorbed, the aim was to adjust gas flow and speed of stirring so that approximately 80 per cent of the hydrogen would be used up. The entering and emerging gas streams passed through two flowmeters placed side by side. The capillaries for these were cut from the same piece of tubing, the one on the exit side being just five times as long as the other, so that when the two read the same the absorption was just 80 per cent. The flowmeters were calibrated separately. The results are not so satisfactory as those on ethylation on account of the greater number of variables, but they show the same trend. Two runs were made with different preparations of catalyst, both nickel suspended on infusorial earth. The data from the first run are plotted in Fig. 1 and the results of both are given in Tables II and III. As in the ethylation experiments, the readings were made within a short period of time so as to mimimize the effect of changes due to progressive hydrogenation.

The three determinations in which the hydrogen was entirely absorbed are marked by (*). In these the amounts taken up are much smaller than in corresponding experiments with excess of hydrogen.

Table II—Hydrogenation
(Oil, 250 grams; catalyst, 1.5 grams; 20 per cent nickel)

R. p. M.	Hydrogen, Cc. In	Hydrogen, Cc. Absorbed	Hydrogen, Cc. Per cent	Cc. per 1000 R. p. M.
At 180° C.				
1670	50	25	50	15
2200	50	41	82	19
3300	95	81	86	25
7800	350	298	85	38
10,700	565	475	84	44
13,500	755	633	84	47
13,500	433	433	100	32*
At 185° C.				
5900	433	361	83	61
6800	488	407	83	60
7600	515	425	83	56
7500	242	242	100	32*

Table III—Hydrogenation
(Oil, 250 grams; catalyst, 3 grams; 10 per cent nickel)

R. p. M.	Hydrogen, Cc. In	Hydrogen, Cc. Absorbed	Hydrogen, Cc. Per cent	Cc. per 1000 R. p. M.
At 180° C.				
1580	33.5	27	80	18
1800	56	42	75	23
2240	45	36	80	16
3400	158	126	80	36
7800	362	272	75	35
9000	362	272	75	30
10,200	473	355	75	34
12,850	517	413	80	32*
At 190° C.				
4600	247	198	80	43
7200	427	360	84	50

The following experiments were made on the chlorination of toluene and acetic acid:

Into 400 grams of toluene at 100° C. chlorine was passed while stirring with a silver stirrer at 6000 r. p. m. There was practically total absorption at 1100 cc. per minute, the chief product being benzyl chloride. In the presence of a trace of ferric chloride the gas was absorbed as rapidly as it could be admitted.

Under the same conditions, 6000 r. p. m. and 100° C., 475 grams acetic acid, containing 17.5 grams of red phosphorus which had been rubbed to a paste with a part of the acid, absorbed chlorine as rapidly as it could be conveniently passed in, averaging about 1470 cc. per minute. During the second hour the rate averaged only 715 cc. per minute. At the end of about an hour all the phosphorus had dissolved.

A. P. Strietmann, president of The Biscuit and Cracker Manufacturers' Association, has founded a Research Fellowship at the University of Minnesota on fermentation problems arising in the industry of which he is the head. This research will be conducted in the Department of Biochemistry under the direction of C. H. Bailey. A. H. Johnson has been selected to carry on the work under this fellowship.

Influence of Starch on Strength of Wheat Flour[1]

By J. H. Buchanan and G. G. Naudain

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It has been shown that sizes of starch grains may be measured quickly and accurately by the method described. Tests on seven typical flour samples indicate a relationship between sizes of grains and strength of flours. Smaller starch grains tend to indicate a stronger flour.

Whether this relationship is due to actual colloidal properties of the starch or whether it simply reflects the condition under which the constituents were formed, is yet to be determined.

A POSSIBLE relationship between the starch of wheat flour and flour strength has been suggested by various investigations. Armstrong[2] indicated a variation in sizes of the starch grains of wheat flour. Jago,[3] by viscosity measurements, showed the smaller grains to give greater absorption. With the addition of 20 per cent of starch to flour he found the effect upon the absorption to depend upon the size of the starch grains. The flour, with added rice, showed the greatest absorption, wheat second, and potato the lowest. The sizes of the grains in millimeters were as follows: rice, 0.0050 to 0.0076; wheat, 0.002 to 0.052; potato, 0.06 to 0.10. Baking tests indicated a slight advantage in favor of the starches having the smaller starch grains. Hardy[4] makes this statement:

> The power of dough to retain its shape may be due, in some cases, primarily to the nature and number of starch grains. Whatever the influence of starch grains may be, they operate as passive agents; the active mechanical properties of dough, its tenacity and ductility, are due to the protein in complex gluten.

Snyder[5] believed starch to be without effect in influencing the baking strength. The more recent work of Rumsey[6] shows the value of diastatic enzymes in flour. Collatz,[7] in his study of the effect of addition of diastatic enzymes, arrived at the conclusion that the starch of strong flour was more easily hydrolyzed than that of weak flour.

It is evident that the literature does not give a very definite idea of the importance of starch with regard to strength of flour. Upson and Calvin,[8,9] Gortner and Doherty,[10] and Sharp and Gortner[11] have shown the necessity for a consideration of the colloidal properties of gluten. It was with the idea of determining what the colloidal properties of starch might indicate, with respect to flour, that this problem was undertaken.

EXPERIMENTAL

In this work seven typical flours, upon which baking tests had been run in order to determine loaf volume, were examined for the purpose of determining what influence the size of the starch grains might have. The range of the loaf volumes is given in Table III.

Measurements were made to determine the size of the starch grains in the flours examined. Use was made of a high-power microscope equipped with a micrometer eyepiece. This micrometer was standardized against a Thoma chamber so that each division of the scale corresponded to two microns. With this equipment the sizes of the starch grains may be measured quickly and accurately.

It was found that the starch grains, when examined in this manner, could be grouped in two classes—those having diameters of 7 microns or less, and those having diameters of 8 microns or more. To show the accuracy of the measurements Table I is included. It will be noted that only those grains which would be classed as large are included.

TABLE I—DIAMETER OF LARGE STARCH GRAINS IN MICRONS

	Set 1	Set 2	Set 3
	18	14	12
	8	22	16
	24	16	8
	12	32	24
	24	24	20
	12	20	20
	19	22	12
	10	36	28
	24	22	14
	10	16	36
	16	16	26
	14	20	14
	10	14	12
	12	14	8
	22	22	26
	14	18	8
	16	22	12
	20	12	16
	14	18	14
	18	14	18
	16	13	18
	30	18	16
	22	12	10
	28	12	10
	16	8	26
	20	12	20
	22	12	16
	20	30	18
	14	12	20
	..	16	24
	..	22	22
TOTAL	505	561	544
AVERAGE	17.4	18.09	17.5

In Tables II and III are given the data obtained in the examination of the seven samples of flour. Table II indicates the percentages of starch grains of different sizes as found in the samples. Table III shows the loaf volume, percentage of small grains, and the average size of all the grains in each sample of flour. The sizes are diameters of the grains measured in microns.

TABLE II—PER CENT OF STARCH GRAINS OF DIFFERENT SIZES IN SAMPLE

Diameter of Starch Grains in Microns	Sample Number						
	15	13	1	6	5	2	11
30	1.00	0.60	0.90	1.60	1.90	2.20	4.00
25 to 29	0.90	1.00	2.30	1.60	1.90	2.20	2.90
20 to 24	4.50	3.40	6.00	3.90	5.40	9.90	6.90
16 to 19	5.50	5.50	5.00	5.50	5.80	5.70	6.70
12 to 15	4.00	2.90	2.80	2.90	3.10	1.20	1.30
8 to 11	0.90	0.50	0.50	1.80	2.10	1.00	0.20
0 to 8	83.20	86.10	82.50	82.70	79.80	77.80	78.00

TABLE III—COMPARISON OF LOAF VOLUME WITH PER CENT OF SMALL GRAINS AND AVERAGE SIZE OF ALL GRAINS

Sample No.	Loaf Volume Cc.	Per cent Small Grains	Average Size of All Grains Microns
15	1710	83.20	6.69
13	1640	86.10	6.76
1	1540	82.50	7.16
5	1400	82.70	7.72
6	1415	79.80	6.90
2	1310	77.80	8.21
11	1265	78.00	9.31

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[1] Received April 16, 1923.

[2] Supplement form. Board of Agriculture (England), **17**, 45 (1910).

[3] "Technology of Breadmaking," p. 322.

[4] *Ibid.*, p. 319; Supplement form. Board of Agriculture (England), **17**, 52 (1910).

[5] *U. S. Dept. Agr., Office of Expt. Sta., Bull.* **101**, 56.

[6] American Institute of Baking, *Bull.* **8**.

[7] *Ibid., Bull.* **9**.

[8] *J. Am. Chem. Soc.*, **37**, 1295 (1915).

[9] Nebr. Agr. Expt. Sta., *Research Bull.* **8**.

[10] *J. Agr. Research*, **13**, 389 (1918).

[11] *J. Phys. Chem.*, **24**, 101 (1920).

DISCUSSION

An examination of Tables II and III will show that there is a relationship between the sizes of the grains of starch and the strength of flour. With the exception of Sample 15, the flours fall in an order that would indicate that the greater the percentage of small grains the stronger the flour. Sample 13, with a loaf volume of 1640 cc., has 86 per cent small grains. Sample 1 shows a loaf volume of 1540 cc., and 82.50 per cent small grains. Sample 6 shows a volume of 1415 cc. and 79.8 per cent small grains. Sample 11, with a volume of 1265, shows 78.00 per cent small grains.

A consideration of loaf volume with the percentage of small grains is not sufficient. By comparing Sample 1 with 6, and 2 with 11, we find very little differences in the percentages of small grains. However, an explanation is offered when we take into consideration the average size of all the grains, and the percentages of grains of different sizes. Sample 1, with a greater loaf volume than Sample 6, shows only 0.6 per cent of grains that are 30 microns or greater in diameter, while Sample 6 has 1.6 per cent of grains of that size. Again, Sample 2 shows a greater loaf volume than Sample 11. If the average sizes of all starch grains are examined, it will be found that the average size of Sample 2 is 8.21 microns, while that of Sample 11 is 9.31 microns. Also, Sample 11 shows 4 per cent of the grains having diameters greater than 30 microns, while Sample 2 has 2.20 per cent. It is believed, then, that the size of the starch grains is a factor in determination of strength of flour, with the smaller grains indicating the stronger flour.

In view of conflicting opinions in the literature with regard to the action of various reagents on starch grains of different sizes, it is not so easy to give a reason for the foregoing conclusion. It may mean that smaller grains indicate a better colloidal condition. The colloidal properties of the gluten have been held by Gortner and Doherty[10] and others to be an important factor in the determination of strength of flour. It may be that the properties of the starch simply reflect the conditions under which the various constituents of the wheat berry were formed. Further work is now in progress to determine this point.

Quantitative Aspects of the Kreis Test[1]

By George E. Holm and George R. Greenbank

DAIRY DIVISION, U S. DEPARTMENT OF AGRICULTURE, WASHINGTON, D. C.

The intensity of the Kreis test of samples of an oxidized fat is proportional to the amount of oxygen it has absorbed; or, the amounts of fat necessary for equivalent color intensities are inversely proportional to the volumes of oxygen absorbed.

The intensity of the Kreis test is not proportional to the rancidity or tallowiness of a fat. A rancid fat will give the Kreis test, but many fats that have absorbed large quantities of oxygen show only faint traces of rancidity, or none, yet give intense Kreis tests. Some evidence is found to indicate that oleic may be the only unsaturated acid in fats that gives the Kreis test when autoxidized.

Absorption of free oxygen is not necessary for the production of Kreis test by a fat. Exposure of a fat to light without the presence of free oxygen produces a change which causes a Kreis test.

OF ALL the methods that have been proposed for the detection of rancidity in fats, none has proved of greater value than the phloroglucinol-hydrochloric acid test first studied by Kreis.

Many objections to the use of this test have been raised. Winckel[2] objected to it because it is not specific for aldehydes and ketones found in rancid fats, because the depth of color produced is not proportional to the degree of rancidity, and because the test is too delicate. Kerr[3] ascribes the failure of its widespread application to (*a*) confusion of ideas as to exactly what is meant by rancidity, and (*b*) the fact that when a fat has become rancid its condition is so clearly evident that no chemical test is needed to recognize it. In his work he found that (*a*) all rancid fats give the Kreis test roughly but not in proportion to the rancidity, and (*b*) sweet fats do not give the Kreis test—except, in a few cases, cottonseed oil. He also agrees with Winckel that the test is too delicate and not specific.

Confusion with regard to the status of the Kreis test has been due to the fact that those factors concerned in the production of rancidity and those factors involved in producing the test are not well understood. Quantitative data are therefore lacking.

Rancidity has been ascribed to an oxidation process, and the observation that the presence of air favors the development of rancidity has been confirmed by numerous workers. Wagner, Walker, and Ostermann[4] claim, however, that rancidity can be produced by light in the absence of air.

That air, and especially oxygen, is a factor in the production of rancidity[5] of fats or tallowiness in butterfat has been shown in the work of the authors. Butterfat exposed to the action of oxygen will soon lose its color and give simultaneously a strong Kreis test, and will liberate iodine from potassium iodide in proportion to the amount of oxygen taken up. These and other tests upon the product substantiate the views of Winckel and of Vintelesco and Popesco that peroxides are formed. Oleic acid and triolein acted upon by oxygen give the same characteristic tallowy or rancid odor and the Kreis and iodine liberation tests. These experiments furnished only a qualitative basis for comparison of two fats. Fats were therefore studied quantitatively with reference to the amount of oxygen absorbed.

EXPERIMENTAL

A gastight stirrer was fitted into a flask containing a weighed amount of fresh, dry butterfat. This flask, containing an inlet and an outlet tube, was evacuated and filled with oxygen from a gas buret. The flask was kept at a constant temperature and the stirrer run at high speed, and the volume of oxygen absorbed was noted from time to time. The induction period varied with the freshness of the sample of fat. With fresh butterfat this period was

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[1] Presented before the Division of Agricultural and Food Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] *Z. Nahr. Genussm.*, **9**, 90 (1905).

[3] THIS JOURNAL, **10**, 471 (1918).

[4] *Z. Nahr. Genussm.*, **25**, 704 (1913).

[5] The term rancidity as used throughout this paper excludes hydrolytic changes in the fats.

approximately 3 hours, with lard approximately 1.5 hours, etc. Older samples showed shorter induction periods. Samples were withdrawn through the outlet tube at regular intervals and various tests were performed.

In order to determine the amounts of fat necessary to give Kreis tests of equal intensity, a small amount of each sample was weighed into a small flask and dissolved in a definite volume of ether. Trial tests were made with varying amounts of each sample until the amounts were ascertained which gave equivalent colors with the Kreis phloroglucinol reagent. Prior to the test the ether contained in each tube was evaporated by placing the tube in a water bath kept at 40° to 50° C., since it was found that the absence of ether gave more clear-cut results. The volumes of solution of the samples used for each test ranged from 3 cc., with fats but slightly oxidized, to 0.10 cc., or less in the case of highly oxidized fats. The amount of hydrochloric acid used in each case was 1 cc. As a rule the best results were obtained when the amount of fat used in each test ranged from 0.10 to 0.50 gram.

The iodine liberation test was carried out by ascertaining, in the usual way, the amount of iodine liberated from a slightly acidified potassium iodide solution by 1 gram of fat in 24 hours.

The results obtained upon pure butterfat are found in Table I.

TABLE I—THE PROPERTIES OF A DRY BUTTERFAT (400 GRAMS) THAT HAS ABSORBED VARIOUS AMOUNTS OF OXYGEN AT 95° C.

Oxygen Absorbed Cc.	Acidity *N*/14 HCl per 5 G. Cc.	Iodine No.	Iodine Liberated from KI in 24 Hours by 1 Gram of Fat G.	Kreis Test Amount Necessary for Equivalent Color Intensities G.	*K.* Amounts Fat × Vol. Oxygen	*K.* Basis of 100 Grams Fat
0.00	0.52	31.50	....	Negative	...	...
5.00	0.88	31.44	....	0.20	...	...
300	0.90	30.42	0.0006	0.014	4.20	1.05
500	1.05	30.80	0.0010	0.0090	4.50	1.25
800	1.65	29.18	0.0017	0.0055	4.40	1.10
1100	2.00	28.70	0.0026	0.00385	4.23	1.06

The results shown in this table indicate that in the autoxidation of butterfat there is an increase in the acidity and a decrease in the iodine number. The liberation of iodine from potassium iodide was found to be a slow reaction, but was found to be a comparative measure of oxidations when carried out under similar conditions.

The relation of acidity to oxidation will be discussed in another publication.

With regard to the tests mentioned, it is evident that neither the iodine number nor the iodine liberation test is sensitive enough to detect small changes through oxidation. The intensity of the Kreis test, however, was found to be very marked with small changes in oxidation. Furthermore, *the color intensity is directly proportional to the amount of oxygen absorbed by a fat; or, the amount of a fat necessary to give equivalent colors with the Kreis reagent is inversely proportional to the amount of oxygen absorbed, up to a certain limit.* The rigidity of this proportionality is shown by the figures obtained by the products of the oxygen absorbed and the amount necessary to give the chosen color intensity in each case. Where tests are carried out at various times and where a standard with a fat is difficult to maintain, a methyl red standard at pH 4.8 has been found very convenient for purposes of comparison. Knowing the direct relationship between oxygen absorbed and the Kreis test, it is possible to calculate that in the case of a butterfat that has absorbed 1 cc. of oxygen per gram of fat, 11 mg. are necessary to produce such a color intensity. In case of a fat having absorbed 1 cc. per 100 grams, 1.10 grams should give this intensity. The sensitiveness of the Kreis test and its strict quantitative relationship to the oxygen absorbed make it an exceedingly good measure of the oxygen absorbed, other changes being excluded.

Lard contains a high percentage of unsaturated fatty acids, not oleic. Treating a fresh sample of lard under conditions similar to those used in Experiment 1 on butterfat, it was again found, as shown in Table II, that the intensity of the Kreis test upon samples of oxidized lard was proportional to the amount of oxygen absorbed.

It is noted, however, that for equivalent amounts of oxygen absorbed by butterfat and lard per 100 grams of substance the amount of oxidized lard necessary to give a Kreis test of a certain intensity is greater than the amount of oxidized butterfat.

TABLE II—RELATION OF INTENSITY OF KREIS TEST TO AMOUNT OF OXYGEN ABSORBED BY 450 GRAMS OF LARD AT 95° C.

Oxygen Absorbed Cc.	Kreis Test Weight of Fat Necessary for Equivalent Color Intensities G.	*K.* Cc. of Oxygen Absorbed × Weight for Equivalent Color	*K.* Basis of 100 Grams Fat
90	1.00	90.00	20.00
180	0.60	108.00	24.00
360	0.25	90.00	20.00
540	0.075	40.50	9.00

According to Lewkowitsch[6] approximately 49 per cent of the acids in lard is oleic acid, 10 per cent is linolic acid, and a small fraction is perhaps linoleic. Butter,[7] on the other hand, contains 36 per cent of its acids as oleic acid, and has no other unsaturated acids, as far as known. It will be shown later that the absorption of oxygen by oleic acid does produce compounds that give the Kreis test in a ratio approximately equal to that of butterfat. In view of this fact the foregoing table for lard would tend to show that the oxygen absorbed by lard in this case was taken up largely by the unsaturated linkages not oleic, and that this absorption does not give rise to compounds which produce a Kreis test. Unfortunately, no linolic or linoleic acid was on hand, so that it could not be definitely determined whether or not oxygen absorption by these acids produces compounds capable of giving a Kreis test.

It is extremely important to note here, however, that in no sample used was there more than the slightest trace of rancidity, even after an absorption of 180 cc. of oxygen in 450 grams of lard. If oxidized oleic acid is responsible for the rancid odor in oxidized butterfats, we must assume that in this case unsaturated acids other than oleic are largely involved.

The idea that there can be autoxidation without any noticeable rancidity was contrary to all general belief, and for this reason various other fats and oils were autoxidized and tested. No quantitative results were obtained upon these oils. Cottonseed oil, which gave practically no Kreis test, when autoxidized gave the Kreis test in increasing intensity but showed only a trace of a characteristic rancid odor. This may explain why sweet cottonseed oil will at times give a Kreis test. It is possible that oxygen may be absorbed without a proportional formation of compounds that give a rancid odor, but with a formation of those compounds that give the Kreis reaction.

Olive oil, which contains practically 93 per cent of its liquid acids as oleic acid, and 7 per cent as linolic, was next tried, with similar results.

These results indicate conclusively that for a fat the intensity of the Kreis test is proportional to the oxygen absorbed and is a measure of oxidation, but has no direct quantitative relation to the degree of rancidity as measured by the olfactory senses. That there is no direct quantitative re-

[6] "Chemical Technology and Analysis of Oils, Fats, and Waxes," II, 3rd ed., p. 780.

[7] *Ibid.*, II, 3rd ed., p. 833.

lation may also be shown by absorbing in 110 grams of butterfat 10 cc. of oxygen and comparing this product with 100 grams of butterfat to which have been added 10 grams of butterfat which has absorbed 10 cc. of oxygen. The former will show tallowiness and a Kreis test, while the latter will give a Kreis test of the same intensity but will show little or no tallowy odor, which shows that as oxidation progresses tallowiness and the Kreis test are not developed proportionally. Preliminary tests have shown that mixtures of heptylic aldehyde and pelargonic acid added to fresh fat will produce a condition very similar to tallowiness of butterfat or rancidity of many fats. These compounds and other decomposition products of oxidized fats are undoubtedly the cause of the rancid odors, but neither of the two compounds mentioned above give the Kreis test. As oxidation progresses, therefore, it seems that the compounds giving the tallowy odors are not formed in stoichiometric ratio to the compounds that give the Kreis test. It is possible that as they are formed they are in some cases subsequently destroyed, or that various unsaturated compounds give different decomposition products.

That the oleic acid radical is one constituent that may be concerned in the oxidation and formation of products which give the Kreis test, is shown in the following experiment, where oleic acid was autoxidized.

TABLE III—RELATION OF INTENSITY OF KREIS TEST TO AMOUNT OF OXYGEN ABSORBED BY 300 GRAMS OF OLEIC ACID AT 50° C.

(Standard equivalent = pH 4.8 with methyl red)

Oxygen Absorbed Cc.	Kreis Test Amount Necessary for Equivalent Color Intensities G.	*K.* Weight of Fat Used × Amount of Oxygen Absorbed	*K.* On Basis of 100 Grams of Oleic Acid
60	0.076	4.56	1.52
90	0.050	4.50	1.50
130	0.038	4.94	1.63
175	0.027	4.72	1.57
475	0.010	4.75	1.58

As in the case of the fats and oils tried, the intensity of the Kreis test is proportional to the oxygen absorbed. Under the conditions under which the experiment was carried out there is no direct ratio between the intensity of the tests with butterfat and lard as compared with their oleic acid content when the unit of oxygen absorbed is the same per gram weight of fat. Two samples of the same fat autoxidized may or may not give equivalent weights for the same intensity of Kreis test when equivalent amounts of oxygen have been absorbed. It has been noted, however, that traces of water present affect the course of the reaction, and it is probable that if all fats tried were absolutely dry when autoxidized a definite ratio would be obtained between the Kreis tests and some one constitutional property of the fats.

Kerr[8] states that rancidity "can be absolutely prevented by the exclusion of oxygen." The contention has been made, by a few workers, however, that oxygen is not necessary for the production of rancidity, and this agrees with some further observations that the writers have made. Certain fats when sealed in a vacuum and exposed to sunlight will become rancid and will give a Kreis test. Some fats after prolonged storage without access of light have shown similar properties. It is improbable that the reaction which occurs *in vacuo* is identical with that which takes place when pure oxygen is absorbed. Properties of the color formed with the Kreis reagent indicate this.

Since the change that occurs in a fat that is stored *in vacuo* without access of light is very slow, and since few fats are subjected to the action of light at any time in their handling, it is doubtful if any slight action from this cause will have any bearing upon the Kreis test as previously discussed.

Detailed experimental work upon the nature of the reaction in fats stored *in vacuo* in sunlight will be the subject of another publication.

DISCUSSION

The experiments upon the oxidation of butterfat and lard reported here were carried out at 95° C., and consequently the question might be raised whether the reactions at this temperature would be comparable with reactions occurring at lower temperatures. Because of the time required for these autoxidation reactions at lower temperatures, it is not feasible to use these temperatures. Experiments carried out at 50° C. furnished results that were in good agreement with those reported. Results upon oleic acid at 95° C. agree well with those reported for 50° C.

The constants obtained for butterfat, lard, and oleic acid are of no great comparative value as they stand. They serve to indicate, however, that oleic acid will give the Kreis test in proportion to the amount of oxygen that it has absorbed. The results upon lard would indicate that some acid radical or radicals present in this substance will not give the Kreis test when it absorbs oxygen. Assuming that the Kreis test that is produced when lard is oxidized is due to oxidation of the oleic acid radical, we might conclude that oxidation of linolic or linoleic acid radicals produces no compounds that are capable of giving the Kreis test. While the evidence points strongly that way, it can be determined with certainty only when these compounds are subjected to oxidation and the products are tested.

It is significant to note, however, that in all experiments which have been carried out, no case has been noted where there has been appreciable oxidation without giving a Kreis test. This would indicate that, whatever the acid radicals, in addition to oleic, that give rise to the Kreis test, they oxidize simultaneously with other unsaturated radicals that do not give the test. The fundamental nature of the reactions is evidently the same and the autocatalyst for one is also a catalyst for the others.

This observation makes it quite certain that the Kreis test is always a good measure of the degree of oxidation where at least one radical is present which is capable of producing it under such conditions. This is especially true with butterfat, since the oleic acid radical is probably the only unsaturated radical present. In the case of this fat the test has been used with success to follow oxidation changes during storage.

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[8] *Cotton Oil Press*, 5, 45 (1921).

Carbon Tetrachloride Fire Extinguishers

According to tests made at the Pittsburgh Experiment Station of the Bureau of Mines relative to the hazards to fire-fighters from gases and smoke resulting from the application of carbon tetrachloride extinguisher to electric arcs, burning insulation, or fires such as may occur in electrical apparatus and machinery, it was found that the application of 1 cubic foot of fire extinguisher to electric arcs and burning insulation in a chamber of 1000 cubic feet capacity developed phosgene, chlorine, and hydrogen chloride in quite dangerous concentrations. Carbon tetrachloride vapors, sulfur dioxide, and carbon monoxide were also formed in less dangerous concentrations.

These tests confirm conclusions drawn from previous tests by the Bureau of Mines that it is dangerous to breathe the gases that may be generated from a 1-quart carbon tetrachloride extinguisher applied to a fire in a confined space from which escape is difficult or impossible, and from which the gases would not be removed by ventilation.

So far as is known, carbon tetrachloride extinguishers are the most effective and satisfactory of any that can be applied to electrical fires with safety from shock to the operator. Arcs of 60 amperes direct current and 220 volts and 35 amperes and 500 volts were easily extinguished with a 1-quart carbon tetrachloride fire extinguisher.

Formation of Formic Acid by Caramelization of Cane Sugar[1]

By Stephen G. Simpson

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The numerical results given in this article indicate that (1) formic acid is produced in considerable quantities by the caramelization of sugar; (2) the amount of formic acid produced is governed by the extent of the caramelization, which in turn is determined by the temperature and time of heating; (3) food products which have not been heated above 160° C. should have produced no appreciable amounts of formic acid by caramelization of sugar; (4) knowing the conditions of temperature and time of heating in the preparation of a food product of known sugar content, the amount of formic acid which should be present due to caramelization can be approximately estimated.

Work is being continued with respect to starches and other carbohydrates occurring in food products.

THE detection and determination of formic acid has in the last few years played an increasingly important part in the analysis of food products. The fact that small amounts of the acid inhibit bacterial growth makes it an efficient preservative, and cases have been cited[2] where it has been so used in commercial products. It has been shown that formic acid is also a natural constituent of some foodstuffs. Seeker,[2] for example, finds in jams, sirups, and other similar foods amounts of formic acid ranging from 0.0009 to 0.0130 per cent, and in dark beers and ales containing considerable caramel[3] amounts from 0.0010 to 0.0040 per cent. Whether or not formic acid is a natural constituent of honey, has been the subject of controversy, although Fincke,[4] Farnsteiner,[5] and Heiduschka and Kaufmann[6] have shown that the amount present is in any case less than 0.02 per cent. Kingzett and Woodcock[7] have shown that formic acid is produced by the slow oxidation of some terpenes, which would lead to the possibility of traces being found in products flavored with essential oils, and this has been verified experimentally by Seeker. Apparently, food products which in their preparation have been heated sufficiently to caramelize the carbohydrates they contain, show comparatively high percentages of formic acid. Thus, Seeker[2] finds in coffee extracts amounts of formic acid from 0.060 to 0.111 per cent calculated on the original coffee, and in samples of caramel amounts up to 0.602 per cent. Similar high values were obtained by the writer, and the values listed below show the effect of caramelization on the formic acid content of a few common commercial products.

	Formic Acid Per cent
Coffee, unroasted	0.000
Coffee, roasted	0.221
Cane sugar	0.000
Starch	0.000
Invert sugar sirup	0.026
Caramel	0.404
Oatmeal, charred	0.057
Wheat bran, charred	0.062

Since formic acid may be added to a food product as a preservative, and since in other food products it occurs naturally through caramelization of the sugars contained therein, it becomes of considerable importance to determine the exact conditions of temperature and time of heating which will

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[1] Received May 16, 1923.

[2] Seeker, *J. Assoc. Official Agr. Chem.*, **1**, 210 (1915).

[3] *Ibid.*, **1**, 556 (1916).

[4] *Z. Nahr. Genussm.*, **23**. 255 (1912).

[5] *Ibid.*, **15**, 598 (1908).

[6] *Ibid.*, **21**, 375 (1911).

[7] *Chem. News*, **105**, 26 (1912); *J. Soc. Chem. Ind.*, **29**, 791 (1910).

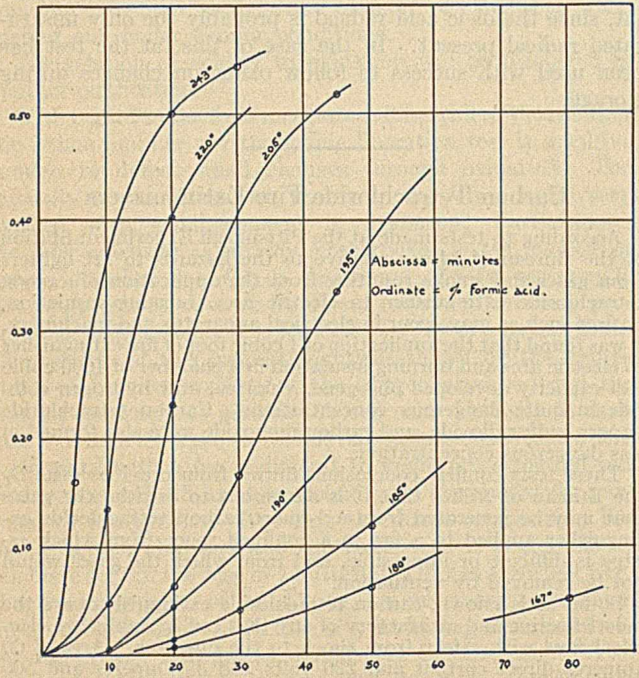

FIG. 1—PRODUCTION OF FORMIC ACID FROM CANE SUGAR BY HEATING AT DEFINITE TEMPERATURES FOR VARYING INTERVALS OF TIME

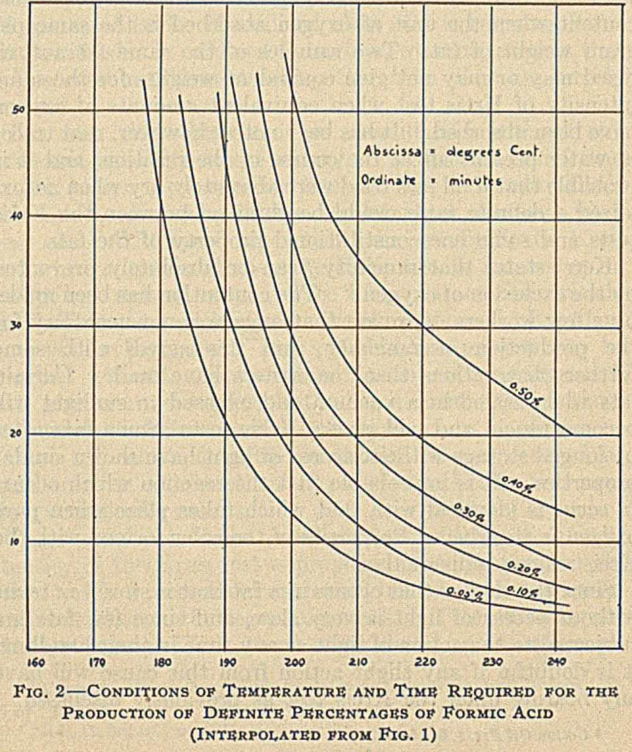

FIG. 2—CONDITIONS OF TEMPERATURE AND TIME REQUIRED FOR THE PRODUCTION OF DEFINITE PERCENTAGES OF FORMIC ACID (INTERPOLATED FROM FIG. 1)

cause the natural formation of formic acid, and to determine the amounts thus formed under these varying conditions. Knowing the conditions of time and temperature under which a food is prepared, it should be possible in many cases to make use of such data to determine whether or not any formic acid which may be found in the product has been added as such, or has been formed by natural changes.

EXPERIMENTAL

Samples of cane sugar, 10.0 grams in each case, were heated in loosely stoppered tubes in an oil bath under varying temperatures and for varying lengths of time. The samples thus prepared were analyzed for formic acid by the Fincke method,[8] which, in brief, consists in steam-distilling 100-cc. solutions of the samples to which 2 grams of tartaric acid have been added. The volume of the sample solution is kept constant by auxiliary heating, and in no case is the volume allowed to decrease appreciably. The vapors are passed through a suspension of calcium carbonate in water and thence through a condenser so that the volume distilled can be determined. After 1500 cc. have been condensed, the calcium carbonate suspension is filtered, the filtrate faintly acidified with hydrochloric acid and boiled 2 hours under a return condenser with 5 to 25 cc. of a solution containing 10 per cent mercuric chloride, 10 per cent sodium chloride, and 15 per cent sodium acetate. The precipitated mercurous chloride is filtered on a Gooch crucible, washed, dried, and weighed. The conversion factor is 0.0975. The results are corrected for a "blank" on the reagents by carrying them through a distillation under conditions identical with the analysis itself.

The values obtained for the caramelized samples of cane sugar are listed in the table, and are also expressed graphically in Figs. 1 and 2.

Temperature ° C.	Time of Heating Min.	Appearance of Sugar after Heating[a]	Formic Acid Mg.	Formic Acid %
145	20	*B*	0.0	0.000
	120	*B-C*	0.6	0.006
167	20	*B*	0.0	0.000
	35	*B-C*	0.0	0.000
	80	*F-G*	4.9	0.049
180	20	*E-F*	0.8	0.008
	50	*G*	6.1	0.061
185	10	*B*	0.0	0.000
	20	*F*	1.3	0.013
	30	*G*	4.0	0.040
	50	*H*	11.9	0.119
190	10	*B*	0.1	0.001
	20	*F-G*	4.3	0.043
195	10	*E*	0.4	0.004
	20	*G*	6.3	0.063
	30	*H*	16.6	0.166
	45	*H*	33.7	0.337
205	5	*C*	0.0	0.000
	10	*F*	4.8	0.048
	15	*G*	6.1	0.061
	20	*G-H*	23.1	0.231
	45	*H*	51.8	0.518
220	10	*H*	13.5	0.135
	20	*H*	40.1	0.401
243	5	*G-H*	16.0	0.160
	20	*H*	50.0	0.500
	30	*H*	54.8	0.548

[a] *A* = Sugar unchanged
B = Slightly yellow but granular
C = Superficially melted
D = Entirely melted, light yellow
E = Entirely melted, deep yellow
F = Entirely melted, light brown
G = Entirely melted, dark brown
H = Entirely melted, black

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[8] *Z. Nahr. Genussm.*, **21**, 1 (1911); **22**, 88 (1912); **23**, 255 (1912); **25**, 386 (1915); *Biochem. Z.*, **51**, 253 (1913).

Chemistry of Wood[1]

VI—The Results of Analysis of Heartwood and Sapwood of Some American Woods

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THIS report contains the results obtained in the analysis of heartwood and sapwood of ten American woods. The work was undertaken to determine whether there is any uniform difference in chemical composition between sapwood and heartwood in either softwoods or hardwoods.

The methods of analysis used are the same as given in the preceding paper in this series.[2] All determinations were made in duplicate and the average is given in Table I.

DISCUSSION OF RESULTS

ASH CONTENT—There is no general agreement in the relative ash content of sapwood and heartwood in the species examined.

EXTRACTIVE CONTENT—In general, the extracts of ether, cold water, hot water, and 1 per cent sodium hydroxide are lower in the sapwood than in the heartwood of the softwoods. In the hardwoods the extractives are lower in the sapwood than in the heartwood of yellow birch, white oak, and yellow poplar, but the reverse is true of white ash and pignut hickory. Thus, from the standpoint of extractive content in sapwood and heartwood, the hardwoods analyzed are divided into two classes—one class following the order of the softwood, the other following the reverse course.

ACETIC ACID—The acetic acid obtained by hydrolysis is higher in the sapwood than in the heartwood of both classes of woods.

METHOXYL CONTENT—The relative percentages of methoxyl in the sapwood and heartwood of the species analyzed cannot be arranged in any general order.

PENTOSAN CONTENT—There is a tendency toward higher yields of pentosans in the sapwood than in the heartwood of the species examined. The difference in yields, however, is slight.

METHYL PENTOSAN CONTENT—The methyl pentosan content in sapwood and heartwood of the same class is quite uniform.

CELLULOSE CONTENT—For the relative cellulose content of sapwood and heartwood, the species analyzed, with the exception of yellow poplar, are grouped in a manner similar to that for extractives. All the softwoods examined have higher cellulose yields in the sapwood than in the heartwood. This tends to counterbalance the low extractives in the sapwood. One hardwood group, yellow birch and white oak with high extractives in the heartwood, has high cellulose content in the sapwood. The other group of hardwoods, white ash and pignut hickory with high extractives in the sapwood, has high cellulose content in the heartwood. The results obtained from the two yellow poplar samples, which are an exception to the foregoing scheme of grouping, can be explained by referring to the condition of the samples.

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[1] Presented before the Division of Cellulose Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] THIS JOURNAL, **14**, 1050 (1922).

TABLE I—ANALYSES OF SAPWOOD AND HEARTWOOD OF SOME AMERICAN WOODS
(Results in percentage of oven-dry (105° C.) samples)

				Solubility in										In Cellulose				
Species	Sample	Moisture	Ash	Cold Water	Hot Water	Ether	1% NaOH	Acetic Acid	Methoxyl	Pentosan	Methyl Pentosan	Cellulose	Lignin	Pentosan	Methyl Pentosan	Alpha	Beta	Gamma
White ash:																		
No. 2 sapwood	179	5.34	0.61	5.81	6.41	1.17	21.77	3.23	4.70	19.85	2.40	50.38	26.95	18.83	1.60	74.67	13.67	11.66
No. 2 heartwood	180	5.45	0.30	2.24	3.40	0.43	19.59	2.31	5.36	19.90	2.25	53.56	27.39	16.75	1.34	64.68	24.58	10.84
No. 3 sapwood	181	4.91	0.57	5.25	7.02	0.88	21.93	3.70	5.66	20.16	2.63	49.72	27.39	19.67	1.60	55.11	28.29	16.50
No. 3 heartwood	182	7.42	0.32	2.12	4.46	0.46	18.97	2.66	5.20	19.87	2.46	53.40	28.38	17.34	1.47	42.45	33.22	24.33
Yellow poplar:																		
No. 1 sapwood	187	4.30	0.48	1.29	1.98	0.27	16.74	3.12	5.81	18.37	3.28	58.13	23.08	15.52	2.21	50.13	30.74	19.13
No. 1 heartwood	188	3.79	0.39	1.50	2.08	0.43	17.70	2.89	5.86	18.47	3.11	59.57	22.19	14.97	2.40	61.30	20.20	18.50
No. 2 sapwood	189	3.79	0.36	1.45	2.51	0.13	16.91	3.33	5.89	18.82	1.22	58.02	23.86	19.01	0.78	34.32	48.52	17.16
No. 2 heartwood	190	3.88	0.33	1.45	2.89	0.58	17.57	2.73	6.03	19.08	1.13	59.47	23.69	17.83	1.47	36.67	42.75	20.58
Pignut hickory:																		
No. 1 sapwood	191	3.54	0.40	4.91	6.45	0.29	19.11	3.58	5.56	18.18	1.11	56.08	21.87	16.90	1.30	51.55	21.92	26.53
No. 2 heartwood	192	3.90	0.45	2.07	2.95	0.36	15.10	3.08	5.79	18.64	1.02	58.81	22.85	16.20	1.39	59.44	23.74	16.82
Yellow birch:																		
No. 1 sapwood	207	4.92	0.26	1.05	1.98	0.48	16.77	2.34	5.66	21.36	1.66	58.91	24.69	20.72	1.13	52.15	32.90	14.45
No. 1 heartwood	208	4.76	0.40	4.16	5.69	0.81	20.51	1.78	5.46	20.37	1.39	56.88	24.62	21.87	1.12	61.17	23.23	15.60
No. 2 sapwood	213	4.28	0.18	1.74	2.10	0.88	19.78	3.75	5.47	22.30	1.82	56.57	27.76	22.19	1.71	52.40	26.82	20.78
No. 2 heartwood	214	4.36	0.23	2.76	3.96	0.99	21.14	2.83	5.27	23.21	1.07	54.93	28.13	21.81	1.04	53.56	25.00	21.44
White oak:																		
No. 1 sapwood	209	7.71	0.57	2.55	4.11	0.46	21.11	3.44	5.95	23.25	0.90	49.53	32.34	24.74	0.88	68.07	15.27	16.66
No. 1 heartwood	210	7.70	0.43	7.33	10.15	0.71	25.81	2.59	6.18	21.82	1.57	48.68	32.74	24.22	0.58	67.33	11.84	20.83
No. 2 sapwood	211	7.09	0.37	4.27	5.73	0.65	21.69	2.47	6.02	21.72	0.94	53.18	31.14	24.81	1.20	53.81	22.63	23.56
No. 2 heartwood	212	6.99	0.42	4.76	6.60	0.62	22.67	2.97	5.64	22.08	0.91	52.12	31.30	24.54	0.96	52.96	20.41	26.63
Bald cypress:																		
No. 1 sapwood	183	4.72	0.48	0.72	1.42	0.23	8.55	0.77	4.35	8.03	4.38	54.86	35.01	6.25	1.85	76.09	5.93	17.98
No. 1 heartwood	184	5.30	0.30	2.79	2.99	4.87	10.59	0.48	3.94	6.67	4.49	53.10	33.06	5.84	1.80	76.83	3.94	19.23
No. 2 sapwood	185	6.72	0.86	1.76	2.30	2.80	10.63	0.65	4.99	9.23	3.34	50.94	35.31	5.89	1.65	58.18	26.91	14.91
No. 2 heartwood	186	4.72	0.95	3.27	3.49	7.93	13.56	0.29	4.07	7.88	3.36	49.18	32.27	6.33	1.25	57.38	24.75	17.87
White pine:																		
No. 1 sapwood	193	3.90	0.23	3.55	5.15	5.46	17.16	1.68	4.16	9.31	2.14	54.25	26.51	6.81	2.09	54.56	17.47	27.97
No. 1 heartwood	194	2.92	0.42	5.97	7.68	3.62	19.15	1.43	4.60	8.56	1.00	50.23	26.14	7.12	2.02	57.29	22.42	19.29
Yellow cedar:																		
No. 1 sapwood	195	3.97	0.28	2.13	3.41	1.00	11.72	2.05	4.40	8.47	1.75	58.12	29.03	7.60	2.44	54.61	26.59	18.80
No. 1 heartwood	196	4.00	0.18	2.88	4.12	1.32	12.77	1.53	4.81	8.69	1.85	56.08	28.73	7.78	2.73	...	20.17	...
White cedar:																		
No. 2 sapwood	197	5.59	0.64	2.18	2.82	..	11.02	1.17	5.07	11.61	0.94	55.77	29.85	10.35	1.77	73.78	0.99	25.23
No. 2 heartwood	198	6.39	0.21	1.94	3.22	..	11.41	0.84	5.00	10.79	1.72	55.19	31.39	8.52	1.58	61.47	22.23	16.30
No. 3 sapwood	199	6.02	0.48	3.02	3.96	1.44	12.71	1.11	5.23	10.82	1.16	55.02	32.14	8.95	1.28	69.17	14.04	16.79
No. 3 heartwood	200	6.48	0.27	2.80	4.01	1.87	14.14	0.74	5.09	10.36	1.56	54.42	32.42	7.97	1.32	55.22	24.74	20.04
Incense cedar:																		
No. 1 sapwood	205	6.46	0.47	1.92	2.97	0.67	11.16	1.33	5.95	12.08	0.45	49.09	34.73	10.14	1.24	50.69	12.98	36.33
No. 1 heartwood	206	7.27	0.30	4.74	7.08	4.78	19.99	0.68	6.21	12.04	0.56	44.53	33.67	11.68	1.31	66.62	11.05	22.33

Both yellow poplar samples showed slight signs of decay in the sapwood. This condition would tend to increase extractives in the sapwood. The results show slightly higher extractives in the heartwood than in the sapwood, which indicates that on the basis of extractives yellow poplar is strictly a member of the first group of hardwoods. If it belongs to the first group, the cellulose content should be higher in the sapwood than in the heartwood, which is not the case. This can also be explained on the basis of the decayed condition which decreases the cellulose content in the sapwood, the reverse of what would be expected in sound yellow poplar.

LIGNIN CONTENT—In softwoods, with the exception of white cedar, the lignin content is higher in the sapwood than in the heartwood. In the hardwoods all species except yellow poplar have a higher lignin content in the heartwood than in the sapwood.

A study of the ratio between methoxyl and lignin is shown in Table II. A study of the results reveals the fact that the methoxyl-lignin ratio is approximately 50 per cent higher in hardwoods than in softwoods. This ratio averages less than 13 per cent in bald cypress. In Paper V of this series[2] it was shown that the methoxyl content of isolated redwood and live oak lignins was approximately 17.5 per cent. Bald cypress lignin could not meet these specifications and, consequently, it must differ in chemical composition from redwood and live-oak lignins.

PENTOSAN CONTENT OF CELLULOSE—The pentosan content has a slight tendency to run higher in the sapwood cellulose than in the heartwood cellulose, similar to the results obtained in the original wood.

METHYL PENTOSAN CONTENT OF CELLULOSE—In general, the methyl pentosan content is slightly higher in the heartwood cellulose than in the sapwood cellulose. A similar relation was found in the heartwood and sapwood of the original samples.

α-, β-, AND γ-CELLULOSE CONTENT OF CELLULOSE—The percentages of the three kinds of cellulose in sapwood and heartwood cellulose cannot be grouped in any definite arrangement.

CONCLUSIONS

From a study of the data given in this report the following conclusions may be drawn:

1—In softwoods the water, ether, and alkali extracts are higher in the heartwood than in the sapwood, and as a result the cellulose and lignin are correspondingly lower in the heartwood (except lignin in white cedar).

2—On the basis of extractives hardwoods are divided into two groups: (*a*) those with high extractives in the heartwood, and (*b*) those with high extractives in the sapwood. The former have high cellulose content in the sapwood; the latter in the heartwood.

3—Acetic acid by hydrolysis is higher in the sapwood than in the heartwood of both softwoods and hardwoods.

TABLE II—RATIO OF METHOXYL TO LIGNIN ON OVEN-DRY (105° C.) WEIGHT OF THE WOOD

		Lignin		CH_3O		$\frac{CH_3O \times 100}{\text{Lignin}}$	
Species	No.	Sapwood	Heartwood	Sapwood	Heartwood	Sapwood	Heartwood
White ash	2	26.95	27.39	4.70	5.36	17.4	19.5
	3	27.39	28.38	5.66	5.20	20.0	18.3
Yellow poplar	1	23.08	22.19	5.81	5.86	25.2	26.4
	2	23.86	23.69	5.89	6.03	24.7	25.4
Black hickory	1	21.87	22.85	5.56	5.79	25.4	25.3
Red alder	1	25.97	25.68	2.29	5.33	20.4	20.1
	2	26.64	25.94	5.26	5.26	19.8	20.3
Bald cypress	1	35.01	33.06	4.35	3.94	12.4	11.9
	2	35.31	32.27	4.99	4.07	14.0	12.6
Eastern white pine	1	26.52	26.14	4.16	4.60	15.7	17.6
Yellow cedar	1	29.03	28.73	4.40	4.81	15.1	16.7
Southern white cedar	2	29.85	31.39	5.07	5.00	17.1	15.9
	3	32.14	32.42	5.23	5.09	16.2	15.7
Incense cedar	1	34.73	33.67	5.95	6.21	17.1	18.4

Furfural from Corncobs[1]

III—Effect of Catalysts on Furfural Yield in the Steam Digestion Process

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Laboratory experiments were made to determine the effect of employment of small amounts of catalysts. With hydrochloric, sulfuric, and phosphoric acids a marked increase of furfural yield was obtained when quantities of acid added were sufficient to neutralize the natural base of the cobs. Larger quantities did not give a proportionate increase. The effect of the mineral acids is probably due largely to the organic acids, especially formic, which are liberated. Direct addition of formic acid produced a somewhat greater increase in yield than did the mineral acids. Sulfurous acid gave results comparable with those obtained by formic acid, indicating that the presence of a reducing agent increases the yield. From an economic standpoint the sulfuric and sulfurous acid catalysts seem to offer the most promise.

Semicommercial runs using the sulfuric acid catalyst gave furfural yields of about 9 per cent, 50 per cent higher than those obtained in steam digestion without catalysts. The small amount of acid used does not require neutralization, and there is no increase in steam requirement for the process. Hence, the catalytic process offers considerable commercial advantage.

A PROCESS for producing furfural from corncobs by steam digestion and the development of this process through the semicommercial stage have been discussed in previous articles of this series.[2] The yield obtained under the optimum conditions determined was slightly over 6 per cent of the air-dry weight of cobs used, or about one-third of that theoretically obtainable.

Owing to the simplicity of the operations, low cost of the digestive agent employed, and short reaction period, furfural can be produced more cheaply by this process than by any other yet described. If the yield could be increased without material change in the conditions of the process, for instance by the addition of catalysts, even more economical production would be possible.

The catalysts first suggesting themselves were the mineral acids heretofore used in various methods for the production of furfural. The use of mineral acids as catalysts in the production of furfural from wood waste is referred to in several French patents,[3] but with no significant quantitative data. The organic acids, formic and acetic, which are by-products of the steam digestion process, also present themselves for consideration. The effect of the addition of small quantities of these agents was tested, using the apparatus and optimum conditions worked out where superheated water alone was the digesting agent.

Laboratory Experiments

Mineral Acids—The use of mineral acids, especially sulfuric and hydrochloric, for the production of furfural from pentosan-containing materials is too well known to require special mention in this article. The usual quantitative analytical method involves the distillation of the material with at least two hundred times its weight of strong hydrochloric acid, and consequently is impracticable for the preparation of furfural. Acid digestion methods described for the preparation of furfural[4] give considerably less than theoretical yields and require large quantities of reagents. The cost of such reagents, the operations necessary for their neutralization, and the special apparatus required, make such processes expensive. It seemed probable, however, that the use of very small quantities of mineral acids would result in increased yields under the conditions of the steam digestion process without involving the disadvantages mentioned.

All the catalytic experiments were made under conditions comparable with those in which water alone was the digestive agent.

Except where otherwise noted the conditions were the following:

Eight hundred grams of broken cobs are heated for 30 minutes in a copper autoclave at 180° C. with 4800 cc. of water. The temperature is held constant for 90 minutes longer while a slow distillation is maintained. The distillate collected (2700 to 3000 cc.) is measured and the furfural is determined in an aliquot part. To the weight of furfural in the distillate is added the weight of free furfural found in the liquid remaining in the autoclave and the yield is calculated from their sum. In the experiments described the catalyst was added to the water used for the charge.

The results obtained where small quantities of sulfuric, hydrochloric, and phosphoric acids were used are shown in Table I. The yields in all the tables are calculated from analysis, using the phloroglucinol method. Although they are somewhat higher than the true yield, which may be considered as slightly above 90 per cent of the values given, they are entirely satisfactory for comparative purposes.

Table I—Effect of Mineral Acid Catalysts on Furfural Yield
(Conditions: 800 grams cobs; 4800 grams water; time of digestion, 120 minutes; temperature, 180° C.)

Mineral Acid	Weight of Catalyst: Grams	Weight of Catalyst: Per cent of Cobs	Weight of Catalyst: H Equivalents	Furfural Yield (Based on Air-Dry Weight of Cobs) Per cent
None	....	....	....	8.9
H_2SO_4	4.0	0.50	0.08	9.8
	4.5	0.56	0.09	10.2
	6.0	0.75	0.12	10.8
	6.0	0.75	0.12	11.0
	12.0	1.50	0.25	10.9
	24.0	3.00	0.49	10.7
	80.0	10.00	1.63	7.7
HCl	2.3	0.29	0.06	10.2
	4.4	0.55	0.12	11.3
	8.8	1.10	0.24	11.8
	17.0	2.13	0.48	10.0
H_3PO_4	8.0	1.00	0.16	11.2

The addition of the acid catalysts results in a marked increase in yield. For instance, by the addition of 6 grams of sulfuric acid equal to 0.75 per cent of the weight of cobs, the average furfural yield obtained is 10.9 per cent, as compared with 8.9 per cent where water alone is used.

Several experiments were made to determine whether the presence of the small quantities of sulfuric acid used had any effect on the optimum conditions as determined for the steam digestion process. The temperature, heating period, and water–cob ratio factors were each checked up while the other conditions were kept constant. With a temperature of 170° C. a furfural yield of 7.7 per cent was obtained, as compared with 10.9 per

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[1] Received July 13, 1923.

[2] This Journal, **15**, 499, 823 (1923).

[3] Raisin, French Patent 446,871 (October 12, 1911); A. and E. Lederer, French Patent 464,608 (January 16, 1913); Classen, French Patent 518,140 (April 22, 1919).

[4] Goissedet and Guinot, French Patent 495,116 (May 8, 1917); Ricard, U. S. Patent 1,322,054 (November 18, 1919); Monroe, This Journal, **13**, 133 (1921); Adams, Conant, Clarke, and Kamm, "Organic Syntheses," Vol. I, **1921**, p. 49, John Wiley & Sons, Inc. An acid digestion method is being used for the commercial production of furfural from oat hulls by the Miner Laboratories of Chicago [*Chem. Met. Eng.*, **27**, 300 (1922)], but details of the process have not been published.

cent at the optimum temperature of 180° C. Using a 90-minute heating period (instead of one of 120 minutes), the yield was 9.8 per cent. Decreasing the volume of charge water from 4800 to 3900 cc. lowered the yield to 10.5 per cent. These experiments indicate that with small quantities of catalysts the conditions adopted for the steam digestion process give the most satisfactory results.

Phosphoric acid seems to affect the yield in about the same degree as sulfuric acid. For commercial applications the present high cost of phosphoric acid would eliminate it from consideration. Hydrochloric acid in the lower concentrations gives slightly higher yields than sulfuric acid, but when the concentration of acid is as high as 2 per cent of the weight of the cobs, the sulfuric acid catalyst gives the better yield. Of these two acids, sulfuric would probably be more economical.

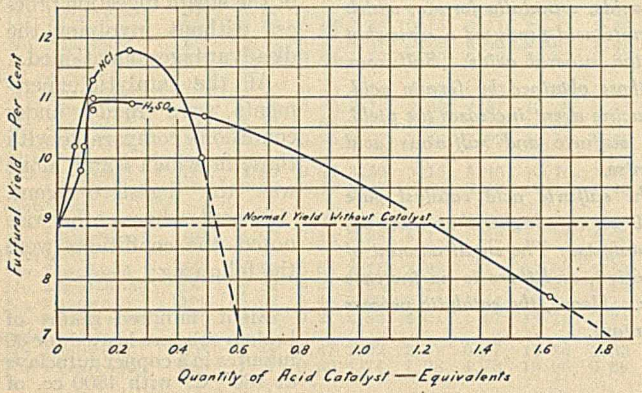

FIG. 1—EFFECT OF SULFURIC AND HYDROCHLORIC ACID CATALYSTS ON FURFURAL YIELD

By plotting the yield against the quantity of acid used, in terms of equivalents, the yield curves shown in Fig. 1 were obtained. The yield with either catalyst increases greatly with the small quantities of acid, but with the larger quantities the increase is not proportionate. In the case of sulfuric acid a quantity equal to 10 per cent of the weight of cobs causes a considerable decrease in the furfural yield.

The sulfuric acid catalyst curve (Fig. 1) has a sharp inflection at the point corresponding to 0.12 equivalent of acid (equal to $49 \times 0.12 = 6$ grams). When this or a smaller quantity of acid was employed, the liquids left in the autoclave, when tested with indicators, showed no free mineral acid. When more catalyst was used, free mineral acid was present. It may be assumed, therefore, that at the point of inflection of the curve sufficient acid has been added to correspond to the natural bases present in the cobs. This assumption was verified by an actual determination of the base. It was found that basic material calculated to be present in the ash of 800 grams of cobs corresponded to about 0.12 equivalent weight of acid.

Forty grams of cobs ashed in a platinum dish at low red heat gave 0.6000 gram of ash. The ash was warmed with a measured quantity of standard acid and the solution titrated. For neutralization of the bases present, 30.4 cc. of 0.2 *N* acid were required. The 40 grams of cobs taken therefore correspond to 0.00608 equivalent, or 0.122 equivalent weight of acid corresponds to 800 grams of cobs.

In the case of the hydrochloric acid catalyst, the curve likewise begins to flatten at 0.12 equivalent, but the peak is not reached until about 0.24 equivalent of acid is present. Beyond this point the yield decreases much more rapidly than is the case with sulfuric acid.

Apparently, where quantities of mineral acids not in excess of the quantity corresponding to the base present in the cobs are employed, their effect is chiefly due to the liberated organic acid which would otherwise be neutralized, rather than to any direct effect which they themselves may have. The quantity of organic acid ordinarily obtained in steam digestion is between 4 and 5 per cent of the weight of cobs. In one case analysis showed the organic acid to comprise acetic and formic acids, 3 and 1.4 per cent of the weight of cobs, respectively. The addition of a base would neutralize part of the organic acids and a decrease in yield might be expected. In one experiment a base in the form of sodium carbonate, in quantity equal to about 1 per cent of the weight of the cobs, was added. The resulting furfural yield was only 6.5 per cent, showing that any decrease in the free acid is disadvantageous. The quantity of base added in this case was still too small to neutralize all the acid formed in the process.

ORGANIC ACIDS—The belief that the liberated organic acid is an important factor in the increased yield obtained in the experiments described, is supported by the observations of Heuser,[5] who has shown that the quantity of furfural produced on heating xylose under pressure with water is materially increased in the presence of a mixture of acetic and formic acids. He infers that the same effect may be obtained in the case of pentosan-containing materials. Several experiments were made to test the effect of these acids as catalysts in the steam digestion of corncobs, and the data obtained are given in Table II.

TABLE II—EFFECT OF ORGANIC ACID CATALYSTS ON FURFURAL YIELD
(Conditions: Same as for Table I)

ORGANIC ACID	WEIGHT OF CATALYST		Furfural Yield (Based on Air-Dry Weight of Cobs)
	Grams	Per cent of Cobs	Per cent
None	..	...	8.9
Acetic	16	2.0	9.0
	20	2.5	9.4
Formic	15	1.9	12.0
	40	5.0	11.1
Acetic plus Formic	(24) (11)	(3.0) (1.4)	9.8

Experiments using quantities of acetic acid varying from 2 to 2.5 per cent of the weight of cobs produced only slight increases in yield. Thus, a furfural yield of 9.4 per cent was obtained in the presence of 2.5 per cent of acetic acid, as compared with 8.9 per cent where water alone was used.

On the other hand, formic acid produced a striking increase in yield. By using 15 grams of acid to 800 grams of cobs (slightly less than 2 per cent of the weight of cobs) a furfural yield of over 12 per cent was obtained. Larger quantities of this acid do not seem to improve the yield, which was only 11.1 per cent when 5 per cent of formic acid was used.

A much smaller quantity of added formic acid than that indicated above will produce nearly as large a yield if a quantity of sulfuric acid equivalent to the base present in the cobs is added at the same time. In one case the employment of 5 grams of formic acid (0.63 per cent) with 6 grams of sulfuric acid gave a yield of 11.7 per cent. From a practical standpoint, however, it would not be economical to use even this smaller quantity of formic acid.

When a combination of acetic and formic acids was added in quantities equal to that normally produced in the steam digestion process—3 per cent and 1.4 per cent, respectively—a 9.8 per cent yield of furfural was obtained. This experiment suggests the possibility, in large-scale practice, of using the mixture of dilute organic acids produced as a by-product in one digestion as part of the charge in subsequent digestions. In this way an appreciable quantity of formic acid could be made available economically.

REDUCING AGENTS—The results obtained indicate that formic acid plays an important role as a catalyst in the production of furfural. Since its effect is apparently different from that of other acids, the question arises if, in addition to its acidity, some other property is not partly responsible for

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[5] *Z. angew. Chem.*, **27**, 654 (1914).

its action. Formic acid differs from the other acids mentioned in that it is a reducing agent, and as such might protect the furfural from oxidation and accompanying polymerization during the digestion process.

Since from an economic standpoint formic acid seemed to be unsuitable as a reducing catalyst, consideration was given to the use of a cheaper agent, such as sulfur dioxide. Experiments employing various quantities of this reagent were made. The results obtained are shown in Table III. In all cases sulfuric acid also was added in quantities sufficient to neutralize the natural base of the cobs, and the yields observed must be compared with the yield (about 10.9 per cent) obtained with the sulfuric acid alone. The addition of sulfur dioxide in quantities up to the point where about 2.4 per cent of SO_2 is present results in increased yields of furfural. At this point the yield is 12.3 per cent, or an increase of 1.4 per cent. Larger quantities of sulfur dioxide cause a decrease in yield, as shown in the table. This observation is in agreement with the fact that comparatively little furfural results from the treatment of pentosan-containing woods by the sulfite process. Since the cost of sulfur dioxide is low, it might be feasible to employ it as a catalyst in the commercial manufacture of furfural.

TABLE III—EFFECT OF COMBINED SULFURIC AND SULFUROUS ACIDS ON FURFURAL YIELD
(Conditions: Same as for Tables I and II)

CATALYST		Proportion of SO_2 to Cobs Weight, Per cent	Furfural Yield (Based on Air-Dry Weight of Cobs) Per cent
Grams H_2SO_4	Grams SO_2		
6	..	..	10.9
6	8	1.0	11.6
6	19	2.4	12.3
6	40	5.0	10.0

MISCELLANEOUS CATALYSTS—Several neutral salts of the inorganic acids were tried as catalysts. Of these, sodium sulfate and zinc chloride in small quantities had no effect, while sodium bisulfite decreased the yield.

The adverse effect of iron in the steam digestion process has been mentioned in a previous article.[6] In cases where sulfuric acid in quantity equivalent to that of the base was employed, a similar decrease in furfural yield in the presence of iron was observed. Thus, when a sheet-iron lining was placed in the autoclave, no other change being made in the conditions, the yield was 7.9 per cent instead of 10.9 per cent.

CONCLUSIONS FROM LABORATORY EXPERIMENTS—The yield of furfural may be materially increased by adding to the charge a quantity of sulfuric acid equivalent to the quantity of the natural base of the cobs. This change is entirely practicable, since the cost of the acid would be negligible. Moreover, it is not necessary to neutralize the acid. It very quickly combines with the base of the cobs, so that its effect on the equipment would be slight. The use of formic acid, except where the dilute acid solutions produced in the process are utilized, is excluded for economic reasons. Sulfur dioxide also seems to offer some promise as a catalyst.

SEMICOMMERCIAL RUNS

The laboratory experiments having indicated that sulfuric and sulfurous acids were the most promising catalysts in increasing furfural yield, the next step was to extend the work to a semicommercial scale. Since the special equipment which would be required in the use of sulfurous acid was not available, experiments were limited to tests with sulfuric acid. The runs were made at the Bureau of Chemistry experimental plant, fully described in a previous article.[6]

A charge of 200 to 250 pounds of cobs and four times that weight of water is heated in a steel digester by means of direct steam. During the heating period a slow distillation is maintained. At the end of 2 hours the contents of the digester are discharged, and the solid residue is drained and pressed. Most of the furfural formed in the process is found in the distillate in the form of a 2 to 3 per cent solution. The portion left in the discharge liquor is generally recovered by a separate distillation as a weak solution and is added to a subsequent charge. The furfural is separated from the digester distillate by means of a specially designed column still.

The conditions found most suitable for the steam digestion process are a temperature of 180° C., corresponding to 130 to 135 pounds of steam pressure, and a digestion period of 2 hours. The yield of furfural actually isolated is slightly over 6 per cent of the air-dry weight of cobs used. The same conditions were adopted for the runs in which sulfuric acid was used as a catalyst. The data obtained are given in Table IV.

In three of the runs (2, 4, and 5) sulfuric acid, in quantity equivalent to the natural base of the cobs in the charge, was employed. This quantity is equal to 0.75 per cent of the air-dry weight of the cobs. In Run 3, instead of sulfuric acid, an equivalent quantity of sodium bisulfate was used. The yields given in the table were calculated from analysis of the distillate and discharge liquors. For comparison, data are given for a typical run where no acid was used (Run 1).

The use of the sulfuric acid catalyst increased the yield from 6.4 per cent to an average of 9.6 per cent, approximately a 50 per cent increase. The bisulfate did not seem to be quite as efficient as the sulfuric acid.

The discharge liquor showed no free mineral acids when tested with indicators and no effect of the acid on the digester was noted. Since no neutralization is required, it is entirely feasible to employ quantities of acids of the order mentioned. By using 0.75 per cent of sulfuric acid an increase in furfural yield equal to 3.2 per cent of the weight of cobs was obtained. In other words, a gain of 4.2 pounds of furfural results from the addition of 1 pound of catalyst.

Runs 1, 4, and 5 were made after the digester and steam line had been insulated with an asbestos-magnesia covering, while Runs 2 and 3 were made without this improvement. Runs 4 and 5, where the acid catalyst was used, may therefore be considered as typical from the standpoint of steam consumption, as well as from that of yield.

The steam consumption per unit weight of cobs is, of course, the same with or without the presence of the catalyst.

The steam required for the digestion in any particular run may be calculated by subtracting the quantity of charge water from the sum of the distillate and discharge liquor weights. In the table the values from Runs 4 and 5 are essentially the same as those in Run 1. The quantity of steam necessary to recover the furfural from the discharge liquors and to rectify the digester distillate will be practically the same for all runs since the vol-

TABLE IV—EFFECT OF CATALYST[a] ON FURFURAL YIELD IN SEMICOMMERCIAL RUNS

Run	WEIGHT OF CHARGE Cobs Lbs.	Water Lbs.	Time for Heating to 180° C. Min.	Time of Digestion Min.	Time of Blow-Off (Pressure, 135–5 Lbs.) Min.	Weight of Total Distillate Lbs.	FURFURAL IN DISTILLATE Concentration Per cent	Weight Lbs.	Discharge Liquor Lbs.	Furfural in Discharge Liquor Lbs.	Total Furfural Produced Lbs.	Yield (Based on Air-Dry Weight of Cobs) Per cent
1	225	700	11	120	20	731	1.69	12.3	757	2.0	14.3	6.36
2	215	560	13	120	23	735	2.49[b]	18.3	993	2.5	20.8	9.67
3	214	570	10	120	20	798	2.16	17.2	961	1.7	18.9	8.83
4	224	700	10	120	19	702	2.62	18.4	827	2.8	21.2	9.46
5	229	650	8	120	20	803	2.49	20.0	820	2.3	22.3	9.74

[a] Run 1 is a typical steam digestion run without catalyst. In Runs 2, 4, and 5 sulfuric acid equal to 0.75 per cent of the weight of cobs was added. In Run 3 an equivalent amount of sodium bisulfate was used.

[b] By repeated fractionation in glass of an aliquot of the distillate the amount of furfural actually isolated was equivalent to 2.31 per cent, or 92.8 per cent of the analytical value. From this the actual furfural yield for the run is calculated to be 8.97 per cent.

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[6] THIS JOURNAL, 15, 823 (1923).

umes and concentrations of the liquids handled do not vary materially.[7]

Because of the increased yield, considerably less steam per pound of furfural would be required in the catalytic process.

It has already been shown that the presence of iron decreases the yield of furfural, whether acid is used or not. The semicommercial experiments with the steel digester gave yields lower than those obtained under comparable conditions in the laboratory. It would seem to be advisable in commercial practice, therefore, to employ a digester lined with tile or other inert material. With this improvement it is probable that the yields would closely approach those obtained on a small scale.

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[7] For further data on steam consumption in furfural production see THIS JOURNAL, **15**, 823 (1923).

Preparation of Dicyanodiamide from Calcium Cyanamide[1]

By H. C. Hetherington and J. M. Braham

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This investigation includes a study of the most efficient method for extracting the cyanamide nitrogen from commercial calcium cyanamide, and the determination of the optimum conditions as to temperature and time of treatment for effecting the conversion to dicyanodiamide. The precautions which should be observed in the various steps of the process, and the type of equipment required have been ascertained.

From this investigation it appears that dicyanodiamide can be produced in quantity at a cost not greater than that of many organic compounds which are now used in bulk.

The solubility of dicyanodiamide in water, ethyl alcohol, and ether was also determined.

THE growing interest in the possibilities of dicyanodiamide as a base material in the synthesis of a variety of nitrogen compounds warrants further study of methods for its preparation. Its possibilities have not as yet been fully determined, but it is believed that when it becomes available in quantity at a low price its field of usefulness will be greatly extended.

The source of dicyanodiamide, commercial calcium cyanamide, is already a relatively cheap material, and hence it is in the method of producing dicyanodiamide from it that a decided lowering in cost is to be expected. The production of dicyanodiamide has formed the subject of several patents and other publications, but the literature on this subject does not contain sufficient information to enable one to carry out the process in an efficient manner. The purpose of the investigation here reported was to obtain the information necessary for the development of a process on a technical scale. In addition to laboratory studies, some larger scale experiments were performed, in the course of which 200 pounds of dicyanodiamide were prepared.

The preparation of dicyanodiamide from calcium cyanamide is based on the fact that in a hot alkaline solution cyanamide polymerizes quite readily to dicyanodiamide. Dicyanodiamide can therefore be obtained simply by extracting crude calcium cyanamide with hot water and evaporating the filtrate to crystallization. The principal difficulty in such a process is that cyanamide is converted to a considerable extent into compounds other than dicyanodiamide, resulting in a very low yield.

The main reaction involved in the preparation of dicyanodiamide may be briefly stated as follows. On extracting calcium cyanamide with water the normal salt is hydrolyzed to the acid salt and calcium hydroxide:

$$2CaCN_2 + 2H_2O \longrightarrow Ca(HCN_2)_2 + Ca(OH)_2$$

The acid salt is quite unstable in solution and undergoes a number of changes, depending principally on conditions of temperature and length of storage. It hydrolyzes further, yielding free cyanamide:

$$Ca(HCN_2)_2 + H_2O \rightleftharpoons 2H_2CN_2 + Ca(OH)_2$$

which then in part polymerizes to dicyanodiamide:

$$2H_2CN_2 \longrightarrow (H_2CN_2)_2$$

and in part hydrolyzes to urea:

$$H_2CN_2 + H_2O \longrightarrow CO(NH_2)_2$$

Other compounds, such as melamine, cyanourea, and ammonia, are also produced to a considerable extent when a solution of the acid salt is maintained at a high temperature. It is seen, therefore, that the main problem in preparing dicyanodiamide consists in converting a solution of calcium acid cyanamide, $Ca(HCN_2)_2$, into dicyanodiamide under such conditions that side reactions are reduced to a minimum.

Various modifications of the simple process mentioned above have been proposed which are essentially attempts to accelerate the polymerization reaction, thereby increasing the yield of dicyanodiamide. The catalytic influence of even very small quantities of ammonium hydroxide on this reaction was observed by Haag and Streckers,[2] and later a process for the production of dicyanodiamide was proposed[3] in which as much as one-half mol ammonia per mol of cyanamide is used. In this process a hot solution of calcium acid cyanamide, to which the ammonia has been added, is treated with carbon dioxide, the precipitated calcium carbonate filtered off, and the solution evaporated to the point of crystallization or dryness. The added ammonia is recovered. The use of cyanamides of the heavy metals—for example, zinc cyanamide—as catalysts was proposed by Immendorf and Kappen.[4] Neither of these processes has been developed.

That the rate of polymerization of cyanamide in aqueous solution is at a maximum when undissociated cyanamide and cyanamide ion, HCN_2^-, are present in equivalent proportions, was shown by Grube and Krüger[5] in their study on the kinetics of the polymerization reaction. They concluded that dicyanodiamide resulted from the union of the cyanamide ion, formed by the ionization of a salt such as calcium acid cyanamide, and an undissociated cyanamide molecule. The dicyanodiamide ion thus formed immediately changes, because of its extremely low ionization, to the un-ionized compound through combination with hydrogen ions present in the aqueous solution. A process based on these observations was patented[6] and an investigation on its technical application was made by Grube and Nitsche,[7] who stated that good results could be obtained by it. Results sub-

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[1] Received February 26, 1923.

[2] *Ann.*, **122**, 22 (1862).

[3] D. R. P. 252,273 (1910).

[4] D. R. P. 257,769 (1911).

[5] *Z. physik. Chem.*, **86**, 65 (1913).

[6] Grube and Krüger, D. R. P. 279,133 (1913).

[7] *Z. angew. Chem.*, **1**, 368 (1914).

TABLE I—EXTRACTION OF COMMERCIAL CALCIUM CYANAMIDE WITH WATER

Expt.	Proportion $CaCN_2$ to H_2O	Water Used in Washing Filter Cake Cc.	Temp. ° C.	Time Min.	Total Nitrogen Extracted %	Water-Soluble Nitrogen Extracted %	Total Nitrogen Lost as Ammonia %	Urea %
2	1:2.5	None	100	15	....	....	1.0	....
3	1:2.5	None	100	15	....	....	1.2	....
4	1:2.5	3 100-cc. portions	100	15	76.8	81.6	0.9	....
5	1:4	None	60 to 65	15	75.9	80.5	0.1	....
6	1:4	100	100	15	85.2	90.0	...	12.0
7	1:4	100	60 to 65	15	86.8	92.2	...	3.3
8	1:4	100	60 to 65	15	86.8	92.3	...	4.1
9	1:4	None	60 to 65	15	76.7	81.4	0.1	....
10	1:4	150 cc. (100 and 50)	60 to 65	15	87.3	92.8	0.1	....
11	1:4	90	60 to 65	30	87.0	92.0	...	....
12	1:4	None	60 to 65	30	77.8	82.8	...	....
13	1:4	400	60 to 65	35	89.8	95.4	...	....
14	1:4	None	60 to 65	30	60.4[a]	64.2	...	....
15	1:5	100	60 to 65	30	90.0	95.4	...	....
16	1:5	100	45 to 50	30	89.0	94.4	...	1.2
17	1:5	None	20	30	50.4	53.0	...	....
18	1:5	None	16	40	62.0	65.6	...	....
19	1:7.5	90	60 to 65	30	91.5	97.2	...	....
20	1:7.5	500	60 to 65	45	93.8	99.5	...	....

[a] Wash water from Experiment 13 used for extraction.

stantiating this theory of dicyanodiamide formation were independently presented at about the same time by Morrell and Burgen.[8] An investigation on the hydrolysis and polymerization of cyanamide made at this laboratory[9] further confirmed this ionic theory of dicyanodiamide formation, and also brought to light certain related reactions, particularly urea formation, which were not fully taken into account by Grube and Krüger in their study on the polymerization in the presence of calcium hydroxide. These will be referred to later in this paper.

In the course of the present investigation, preliminary experiments led to the conclusion that satisfactory results could best be obtained by a method based upon the ionic mechanism suggested by Grube and Krüger.[6] It was clearly shown in the experiments of Grube and Nitsche that the use of ammonium hydroxide in maintaining the desired ionic relations was fairly satisfactory from the standpoint of yields obtained, but, as was pointed out by these investigators, the recovery of ammonia would add an undesirable complication to the operation.

The use of the cyanamide of a heavy metal as a catalyst for the polymerization of cyanamide, as proposed by Immendorf and Kappen,[4] was not investigated in the present study, since the work of Grube and Nitsche[7] on zinc cyanamide had shown that it was not very satisfactory.

The essential feature of Grube and Krüger's method is that the concentration of cyanamide ion, HCN_2^-, and undissociated cyanamide, H_2CN_2, be so regulated that there is always present in solution one molecule HCN_2^- per molecule H_2CN_2. The most favorable conditions, particularly as regards temperature and time of treatment, had not previously been satisfactorily established. The effect of temperature on the course of cyanamide transformation is particularly important in this process, as will be shown later. In addition, there is very little information in the literature on the best conditions for the extraction of calcium cyanamide, and hence this operation also was studied in the present investigation.

EXTRACTION OF CALCIUM CYANAMIDE

The most efficient conditions of extracting calcium cyanamide as to quantity of water, temperature, and duration of extraction are, of course, somewhat dependent on equipment available and on the scale of operations. The aim, in general, however, is to secure as complete an extraction of nitrogen as possible with a minimum quantity of water in the shortest possible time, without the transformation of any of the cyanamide into forms other than dicyanodiamide.

The procedure in the extraction experiments was as follows:

One hundred grams of commercial calcium cyanamide were extracted with a measured volume of water in a mechanically stirred vessel for a given time at a temperature controlled to within 2.5° C. except as otherwise noted. A small variation in temperature has but slight effect on the result. At the end of extraction the slurry was immediately filtered on a Büchner funnel and the filter cake washed with a measured volume of water. The filtrate was analyzed for total nitrogen in all experiments, and in some cases urea, cyanamide nitrogen, and calcium were also determined. The evolution of ammonia was noted in all extractions made above room temperature. To determine the loss of nitrogen in this form several extractions were made in a closed system, the ammonia being carried into standard sulfuric acid by a slow current of air.

The calcium cyanamide used in these experiments contained 20.3 per cent total nitrogen, 19.1 per cent "water-soluble" nitrogen, and 19.1 per cent cyanamide nitrogen. By "water-soluble" nitrogen is meant the quantity of nitrogen extracted when 2 grams of calcium cyanamide are agitated with 400 cc. of water in an end-over-end extractor for 2 hours at approximately 25° C.

The results of the extraction experiments (Table I) show that the loss of nitrogen as ammonia is not particularly serious even at 100° C. during a 15-minute extraction, but that the loss as urea is very important at this temperature. Even at 60° to 65° C. for 15 minutes the loss is 3 to 4 per cent. The use of filter-cake wash water for subsequent extractions results in a low extraction, as is seen by comparing Experiments 12 and 14. From these results it appears that in technical operation the extraction of calcium cyanamide with about five times its weight of water at a temperature of 45° to 50° C. for 30 minutes will be found most satisfactory from the standpoint of general economy of operation. The quantity of wash water to be used will depend on the filtering equipment employed, but in the laboratory experiments a weight approximately equal to that of the calcium cyanamide was found desirable. The stirring during extraction should be very vigorous.

An average analysis of the extract obtained under the conditions just mentioned is:

	Per cent
Total nitrogen	3.58
Cyanamide nitrogen	3.31
Urea nitrogen	0.06
Dicyanodiamide nitrogen (by difference)	0.21
Calcium	2.41

from which the following approximate composition was calculated:

	Per cent
Calcium acid cyanamide, $Ca(HCN_2)_2$	7.35
Urea	0.12
Dicyanodiamide	0.32

POLYMERIZATION OF CYANAMIDE

To establish the proper ratio (1:1) of free cyanamide to the ion, HCN_2^-, for a maximum polymerization rate, it is necessary to liberate one-half of the cyanamide, which is combined as calcium acid cyanamide. From the standpoint of availability and cost the choice is practically limited to three acids—namely, hydrochloric, nitric, and sulfuric. The calcium salts of the first two are so soluble that they

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[8] *J. Chem. Soc.* (*London*), **105**, 576 (1914).

[9] Hetherington and Braham, *J. Am. Chem. Soc.*, **45**, 824 (1923).

would remain in the concentrated mother liquor with the other very soluble constituents. Their separation or elimination would be very difficult. The insolubility of calcium sulfate, on the other hand, makes possible an almost complete removal of the calcium from the solution. Sulfuric acid is also relatively cheap, and hence it was the only acid studied in this investigation.

A convenient method of determining the quantity of acid required to establish the desired concentration is to titrate a sample of the extract with sulfuric acid, using methyl orange as an indicator. The extract may also be divided into two equal portions, one portion completely neutralized with sulfuric acid, and the solutions then recombined. A direct measure of the quantity of acid which must be added during the polymerization process is thus obtained.

EFFECT OF TEMPERATURE ON TRANSFORMATION OF CYANAMIDE—Preliminary experiments on the polymerization of cyanamide at temperatures above 85° C. indicated that only about 74 per cent of the nitrogen in solution was converted to dicyanodiamide. Qualitative tests showed that large quantities of urea were formed. To determine the effect of temperature on urea formation, a calcium cyanamide extract having a concentration of 21.76 grams total nitrogen per liter, and containing 0.32 gram urea nitrogen per liter, was treated with such a quantity of sulfuric acid that ionized and un-ionized cyanamide were present in the proper proportions. Aliquots of this solution were maintained at definite temperatures while the required amount of acid was introduced at a uniform rate over a period of 2 hours. The per cent of total nitrogen found in the form of urea at 55°, 70°, 80°, and 95° C. was 3.2, 8.2, 16.5, and 22.8, respectively. The effect of temperature on urea formation is therefore seen to be very pronounced. The cyanamide content of the final solutions was not determined and the ammoniacal silver nitrate test is unreliable in such solutions, but from later experiments it appears that only at the two highest temperatures was the conversion practically complete.

To determine the effect of operating at a moderate temperature two experiments were made at 60° C. using the procedure described above. The cyanamide was determined by precipitation with ammoniacal silver nitrate. Experience in this laboratory has shown that in the presence of urea and dicyanodiamide the silver cyanamide precipitate includes considerable quantities of these two compounds. To avoid errors from this source the silver precipitate was filtered off, washed, dissolved in dilute nitric acid, and reprecipitated by the addition of ammonium hydroxide. The silver in the precipitate was then determined, after thorough washing, by titration with standard thiocyanate. This method has been shown to give very accurate results even in the presence of large quantities of dicyanodiamide and urea. Urea was determined by the urease method.[10] The results are shown in Table II.

TABLE II—CONVERSION OF CYANAMIDE

CONSTITUENT	For 2 Hours		For 4 Hours	
	Grams per Liter of Solution	Per cent of Total Nitrogen	Grams per Liter of Solution	Per cent of Total Nitrogen
Total nitrogen	24.75	100.0	18.74	100.0
Cyanamide nitrogen	7.54	30.0	2.99	16.0
Urea nitrogen	0.76	3.7	1.57	8.4

In a further series of experiments solutions which originally contained 26.2 grams of nitrogen per liter as calcium acid cyanamide were maintained at 60° C. for 4 hours, following closely the precedure of Grube and Nitsche. In Experiments 1 and 2, hydrochloric acid was used as by Grube and Nitsche, while in Experiments 3 and 4, sulfuric acid was used for comparison. The results are shown in Table II*a*.

TABLE II*a*—CONVERSION OF CYANAMIDE

Expt.	Per cent of Total Nitrogen as		
	Cyanamide	Urea	Dicyanodiamide
1	13.5	5.7	80.0
2	12.6	5.9	78.2
3	15.1	3.2	79.8
4	15.4	3.1	78.2

It is evident from the data in the foregoing tables that conversion is far from complete at 60° C., even after 4 hours. In twelve other similar experiments substantially the same results as those given were obtained, and in no case at this temperature was it possible to obtain over 80 per cent conversion to dicyanodiamide in solution. The yields were determined by analysis of the solutions, using the nickelguanylurea method. Grube and Nitsche reported dicyanodiamide yields as high as 89 per cent under these conditions. In view of these results and the known inaccuracy of the older analytical methods for dicyanodiamide, their results are apparently too high.

Owing to the comparatively slow rate of polymerization even at 60° C., it appears that operation at a higher temperature is to be preferred in spite of the increase in urea formation. In several experiments made at 80° C. for 1.25 hours, yields of dicyanodiamide corresponding to about 80 per cent were obtained. It was noted particularly that the percentage of urea formed was nearly as large in 1.25 hours as in 2 hours at 80° C.

The results of a series of experiments designed to determine the yields when operating at 75° C. or higher, are shown in Table III. The solutions used contained 28 to 30 grams of nitrogen per liter. Dicyanodiamide was determined by direct weighing of the carefully crystallized and dried product.

TABLE III—POLYMERIZATION OF CYANAMIDE

Expt.	Time Hours	Temperature ° C.	Yield—Per cent of Nitrogen in Solution Converted to Cyanamide
1	1.5	80 to 85	82.0
2	2	80 to 85	82.4
3	2	75 ± 2	86.4
4	2	75 ± 2	83.3
5	2	75 ± 2	85.2

It is seen from these results that when polymerization is carried out by fractional precipitation of calcium at 75° C. for 2 hours, about 85 per cent of the nitrogen in solution is obtained as dicyanodiamide. Of the remaining 15 per cent about two-thirds is urea.

As compared with operation at 60° C. the advantage of the higher temperature (75° C.) lies not only in the slightly better yield, but especially in the shorter time of treatment required.

To determine the suitability to larger scale operation of the process developed in the laboratory, 200 pounds of dicyanodiamide were made in batches, using 100 pounds of calcium cyanamide at a time. The procedure was as follows:

> The calcium cyanamide was extracted with approximately five times its weight of water at 45° to 50° C. for 30 minutes, the slurry filtered, the filter cake washed, sufficient 60° Bé. sulfuric acid added to combine with one-half of the calcium present, the solution raised quite rapidly to about 75° C., and the acid required for complete neutralization added at a constant rate for 2 hours, the calcium sulfate filtered off, the dilute solution concentrated until dicyanodiamide crystallized rapidly from a sample cooled to approximately 70° C., the solution then cooled, and the crystalline product separated by centrifugation.

The crude dicyanodiamide contains about 6 per cent of impurities, mainly calcium sulfate and urea, but also some melamine. A single recrystallization from water yields a product analyzing better than 97 per cent dicyanodiamide. Unfortunately, the filtering and pumping equipment available for the larger scale work were of a type quite unsuited for the purpose and hence significant data on the efficiency of the process were not directly obtainable. The results indi-

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[10] Fox and Geldard, THIS JOURNAL, 15, 743 (1923).

cate, however, that the method could be adapted to large-scale operation, and that the efficiency reached in the laboratory experiments could also be attained on a large scale with suitable equipment. The experiments emphasized in particular the necessity of rapidly filtering the slurry immediately after extraction is completed, and of treating the filtrate at once with acid, since large quantities of urea are otherwise formed. This effect is readily explained by the known catalytic action of the hydroxyl ion on the hydrolysis of cyanamide.

Although in the majority of experiments the acid was added at a constant rate over the 2-hour period of polymerization, it was found that by adding the acid more rapidly at first, keeping pace quite accurately with the reaction, about 75 per cent of the cyanamide had disappeared in the first 30 minutes. The remaining 25 per cent was not completely converted before 2 hours. Yields of 85 to 87 per cent were obtained in such cases, based on the determination of dicyanodiamide in solution by the nickel-guanylurea method (to be described in a later paper from this laboratory). In view of the comparatively small increase in yield by this variation in procedure and the added difficulty in plant operation of following the course of reaction closely with the addition of acid, there does not seem to be any marked advantage in this refinement.

Some loss of dicyanodiamide during concentration of the converted solutions was observed. To determine the approximate magnitude of this loss, portions of a solution such as is obtained in this process were evaporated at 100°, 80°, and 60° C., under such conditions that they were concentrated to the same volume (appearance of crystals at the highest temperature) in 1.25 hours. The loss of dicyanodiamide at the three temperatures was 3.5, 3.2, and 0.6 per cent, respectively. Maintaining a similar solution at 100° C. for 6.5 hours resulted in a loss of 8.2 per cent. The quantity of melamine present was shown by qualitative test to have increased considerably during concentration. These experiments emphasize the importance of carrying out the evaporation of dicyanodiamide solutions as rapidly as possible and at temperatures as low as practicable.

The combined and concentrated mother liquors from several experiments contained the following:

	Per cent
Total nitrogen	34.4
Cyanamide nitrogen	3.6
Urea nitrogen	3.6
Calcium	1.2
Sulfate	1.0

The solution was reduced to the consistency of a thick sirup, but all attempts to induce crystallization failed. One constituent was separated by its insolubility in alcohol, and identified as melamine sulfate. The presence of a considerable quantity of cyanourea was also shown. Since the nitrogen in the mother liquors represents approximately 15 per cent of the total nitrogen extracted, its recovery as ammonia by autoclaving would be advantageous, particularly if the manufacture of dicyanodiamide were carried out at a cyanamide autoclaving plant.

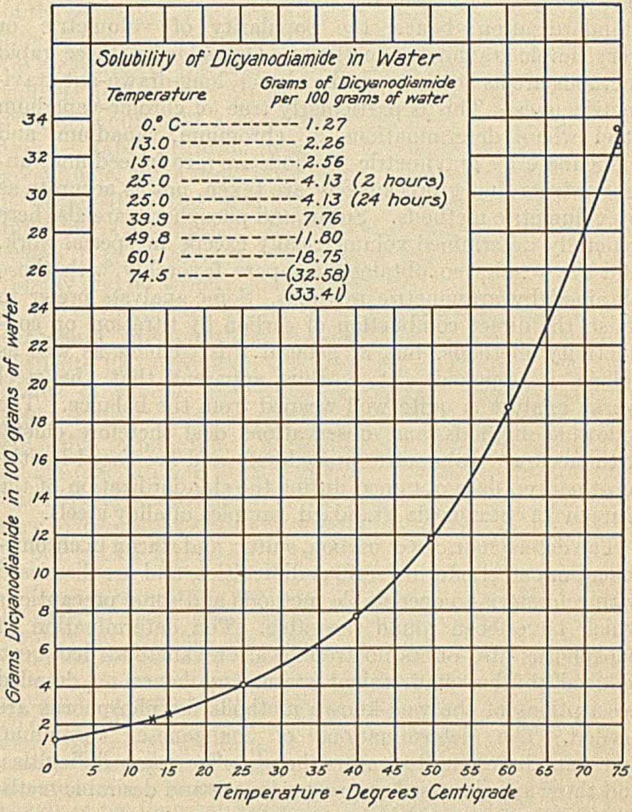
The equipment is very important in this process. Vigorous agitation during extraction, efficient filtration and washing, rather rapid evaporation of the dicyanodiamide solution, and facilities for quickly handling the solutions should be provided. The use of unprotected iron should be avoided, since cyanamide solutions are corrosive.

While an accurate cost estimate on the production of dicyanodiamide cannot be made on the basis of these experiments, there is but little doubt that dicyanodiamide can be produced in quantity at a cost well within the limits of commercial requirements.

SOLUBILITY OF DICYANODIAMIDE IN WATER, ALCOHOL, AND ETHER

The solubility of dicyanodiamide in water, alcohol, and ether was determined, since there is very little information in the literature on this subject. An excess of carefully purified dicyanodiamide was mixed with the solvent in question and agitated for at least 2 hours. In one case the agitation was continued for 24 hours as a check on the shorter period. The results for the two periods were the same. Samples were withdrawn through an alundum-tipped tube, weighed, made up to definite volume, and the nitrogen was determined by the Kjeldahl method.

IN WATER—The results of these determinations are shown in the accompanying graph. The determinations at 13° and 15° C., represented by the crosses, were made by Pohl[11] and Werner,[12] respectively.



IN ALCOHOL AND ETHER—The alcohol used in these determinations had a density of 0.7900 at 20°/4° C. (99.8 per cent); the ether had been dried over sodium and distilled. The results are shown in Table IV.

TABLE IV—SOLUBILITY OF DICYANODIAMIDE IN ALCOHOL AND ETHER

Temperature ° C.	ALCOHOL Grams Dicyanodiamide per 100 Grams Alcohol	ETHER Grams Dicyanodiamide per 100 Grams Ether
0	0.937	0.0006
13.0	1.26[11]	0.01[1]
25.0	....	0.0015
26.4	1.70	....
35.0	2.26	....
35.3	....	0.0026
49.9	3.30	....
60.1	4.13	....

The determinations in ether are not to be regarded as strictly accurate but serve to show the very low solubility of dicyanodiamide in that solvent.

ACKNOWLEDGMENT

The writers wish to express their appreciation of the assistance rendered by Mary A. Kelly and L. A. Pinck in the analytical work in connection with this paper.

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[11] *J. prakt. Chem.*, [2] **77**, 534 (1908).

[12] *J. Chem. Soc.* (*London*), **107**, 726 (1915).

The Analysis of Chrome-Vanadium Steel[1]

By G. E. F. Lundell, J. I. Hoffman, and H. A. Bright

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Particular emphasis is paid to the determinations which are troublesome in the analysis of chrome-vanadium steel—namely, chromium, vanadium, and manganese. The methods which are described and the observations which are recorded are largely the result of work done in the standardization of the Bureau of Standards alloy steel samples by analysts at the Bureau of Standards and in laboratories that have coöperated with the bureau.

In THE analysis of steel works materials, where time is usually of prime importance, methods which will give the required results in the minimum of time are chosen for all determinations other than umpire analyses or primary standardization; hence, the popularity of volumetric or very simple gravimetric methods. Occasionally, these rapid methods are as accurate as the slower, long-drawn-out gravimetric ones. This is particularly true of chrome-vanadium steel where determinations of chromium, vanadium, and manganese by gravimetric methods are rare indeed and, unless extraordinary precautions are taken, not as accurate as by volumetric methods. Sulfur and phosphorus are also here generally determined volumetrically except in special work, and the results so obtained compare favorably with those obtained by gravimetric methods. Some analysts prefer to finish the direct combustion of carbon by titration or conductivity methods, but in general this element as well as silicon is weighed. It is thus apparent that the steel works analyst is quite well weaned from the balance. The following methods and observations deal therefore chiefly with accurate volumetric procedures, and are based for the most part on data obtained during the standardization of the Bureau of Standards standard samples of alloy steels.

The determinations of carbon, sulfur, and silicon in chrome-vanadium steel offer no serious difficulties, and are dismissed with references to acceptable methods and some precautions which have been found desirable. The determination of phosphorus also offers no trouble after vanadium has been reduced to the quadrivalent state, and hence no detailed descriptions of the well-known methods for phosphorus are needed. The determinations of manganese, chromium, and vanadium, on the other hand, offer some difficulties, and these are discussed at greater length and desirable methods which are not widely known are given.

Particular emphasis is placed on the methods used in the analysis of renewal No. 30*b* of the bureau's standard sample of chrome-vanadium steel. The material for this standard was furnished by the Bethlehem Steel Co., South Bethlehem, Pa., and the following firms and analysts took part in its analysis:

Bureau of Standards: The Authors, W. C. Fedde, and C. P. Larrabee
Carnegie Steel Company: Duquesne Works, W. D. Brown, Chief Chemist
Carnegie Steel Company: Homestead Works, John L. Harvey, Chief Chemist
Crucible Steel Company: C. M. Johnson, Chief Chemist
The Cleveland Twist Drill Company: A. S. Townsend, Assistant Metallurgist
Dodge Brothers: Richard B. Hooper, Chief Chemist, H. Morrison, and A. S. Anderson
Illinois Steel Company: South Works, William Brady, Chief Chemist
Ledoux and Company: G. H. Corey and L. R. Shropshire
Cambria Steel Company: H. A. Hosmer, Chief Chemist
Pennsylvania System: M. E. McDonnell, Chief Chemist
Carpenter Steel Company: E. A. Loos, Chief Chemist
Robert W. Hunt & Company: J. H. Campbell

In the analysis of the bureau's standard samples, the coöperating analysts usually employ their own laboratory methods. In addition certain constituents are determined occasionally by methods suggested by the bureau. If a reported analysis is not in close agreement with the general average, the analyst is requested to repeat the determination; the analyses listed under manganese, chromium, and vanadium are all first analyses except those in brackets, which represent successive reports by the same analyst.

CARBON

The determination of carbon presents no special difficulties, and is preferably carried out by direct combustion in oxygen and absorption in soda asbestos, as with plain carbon steel.[2] The following precautions are worthy of special note:

1—The sample should be taken so that errors due to segregation are avoided. Neglect of this precaution is the chief source of error in careful carbon runs.

2—Blanks should be run by heating the boat and lining material in oxygen. It should be borne in mind, however, that the "blank" is the sum of plus or minus errors occasioned by such factors as: (*a*) compounds of carbon in the oxygen, boat or boat lining; (*b*) absorption or loss of water by the weighed reagents; (*c*) diffusion of oxygen from open form absorbers; and (*d*) hygroscopic changes in the weighed system. A normal blank should not run much over 0.5 mg., which represents 0.005 per cent of carbon on a factor weight (2.73 grams). It is interesting to note that a good grade of soda asbestos if used alone will lose water representing 0.01 per cent carbon on a factor weight, and that, owing to the diffusion of oxygen the open type of absorbers, such as the Midvale or Stetzer and Norton, should be weighed at equal times after the flow of gas has ceased. Tests have shown that the loss of weight approximates 0.0001 gram per 10 minutes and that complete diffusion represents approximately 0.05 per cent of carbon on a factor weight.

3—Oxides of sulfur cause positive errors approximating 0.005 per cent carbon in combustions of ordinary steels (0.04 per cent sulfur) and greater errors in high sulfur material. Consequently, steps to avoid these errors, such as using a sulfuric-chromic acid purifier, must be taken where this source of error is of consequence.

4—The burned slag should be examined for evidences of incomplete combustion and the whole combustion operation checked periodically by direct combustion of similar analyzed material, preferably Bureau of Standards steels.

First analyses for carbon in Sample 30*b* ran from 0.280 to 0.301 per cent and final analyses from 0.285 to 0.301 per cent. The maximum variation from the general average (0.292 per cent) was therefore practically ±0.01 per cent carbon. This represents the accuracy that can be expected in umpire determinations of carbon in plain and ordinary alloy steels running up to 1 per cent of carbon. In routine analyses an accuracy to ±0.02 per cent is possible.

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[1] Received May 1, 1923. Published by permission of the Director, U. S. Bureau of Standards.

[2] For detailed descriptions of this method see *Proc. Am. Soc. Testing Materials*, **22**, I, 578 (1922); also "Methods of the Chemists of the U. S. Steel Corporation for the Sampling and Analysis of Alloy Steels," J. M. Camp, chairman, Pittsburgh, Pa., **1921**, p. 9.

MANGANESE

Chromium and vanadium introduce difficulties in the determination of manganese in chrome-vanadium steel, as both undergo valence changes along with manganese in many of the methods which are used for plain carbon steel. Thus, in the bismuthate-ferrous sulfate method, chromium is partially oxidized by the bismuthate and then reduced by ferrous sulfate when the reactions are performed at room temperature, while vanadium is reduced by ferrous sulfate and subsequently incompletely oxidized by permanganate when determinations are carried out rapidly in ice-cold solutions, as in methods designed to avoid interference by chromium. These troubles can be largely overcome by choosing a suitable reducing agent, such as mercurous nitrate as in Kelley's electrometric titration method,[3] or sodium arsenite as in the usual procedure.[4] All the methods, however, possess various drawbacks, as, for example, the difficult end points in procedures employing final titration with arsenite,[5] the uncertainties introduced by the precipitate and by the taking of an aliquot in the zinc oxide precipitation method, the special apparatus needed in the electrometric procedure, and the time consumed and the unpleasant fumes in the Ford method. The results obtained by the electrometric and by the Ford methods leave nothing to be desired. The following method is described because (1) it is very accurate, (2) it is reasonably rapid, (3) it does not possess disagreeable features, (4) it embodies a preliminary separation which is useful in the determination of other constituents of alloy steels, and (5) because it has not been widely published.

In this method chromium and vanadium are precipitated and separated from manganese and the most of the iron at the start. This is accomplished by dissolving the steel in dilute sulfuric acid, carefully adding sodium bicarbonate solution and then filtering. It is to be remembered that all but traces of the iron is in the bivalent state at the time of the bicarbonate addition, and that the latter is never added in sufficient amount to provide free carbonate in the solution. Similar results are achieved through the use of ammonia, as advocated by Johnson.[6] Precipitation by sodium bicarbonate or ammonia (presumably sodium carbonate or ammonium carbonate would do as well) has the advantage of introducing no troublesome reagent such as cadmium in Cain's method.[7] It is superior to precipitation by an emulsion of zinc oxide as in Volhard's method,[8] in that the method is more rapid and the quantitative separation of manganese can be made absolutely certain by a simple treatment of the precipitate. In contrast, uncertainties are introduced in Volhard's method by the volume displacement of the bulky precipitate, possible retention of manganese, and the sometimes doubtful capacities of the volumetric apparatus.

It is interesting to record that, in addition to vanadium and chromium, the bicarbonate precipitate also quantitatively holds such other constituents of alloy steel as aluminium, titanium, zirconium, cerium, and uranium, and that the precipitation separates these from the most of the iron. The bicarbonate or ammonium precipitation of these elements, therefore, quite satisfactorily serves as a rapid substitute for an ether separation. It is also a valuable aid in the detection or determination of traces of these elements in steel in that large amounts of steel can be taken; furthermore, it is superior to an ether separation where vanadium is involved, as there is no question as to the complete separation of vanadium.

BICARBONATE PRECIPITATION METHOD[9]—The success of the bicarbonate precipitation method depends on the addition of the proper amount of bicarbonate and the rapid filtration of the solution. The former can be easily controlled by attention to the preparation of the sulfuric acid solution and careful measuring of the acid. (10 cc. of 10 per cent, by volume, sulfuric acid is used up by 1 gram of pure iron, and a like volume requires 37.5 cc. of the 8 per cent bicarbonate solution.) Rapid filtration depends, of course, on the use of a good funnel and a rapid filter paper. Much quicker filtration is obtained if the precipitate is allowed to settle before filtration is attempted. In the determination of manganese, where 1 gram of sample is ample, the precipitate settles rapidly and no serious oxidation and hydrolysis of iron occurs in the covered flask during this short settling period; in bicarbonate precipitations designed to separate traces of elements like chromium and vanadium (in which 10 to 20 grams of sample and correspondingly larger amounts of acid are used), the precipitate settles less rapidly, and it is advisable to maintain a nonoxidizing atmosphere to prevent undue precipitation of iron during the settling period. Carbon dioxide is convenient for this purpose, and it is only necessary to maintain a stream of the gas over the solution sufficient to prevent back pressure.

PROCEDURE—Treat 1 gram of the sample in a 200-cc. covered Erlenmeyer flask, with exactly 20 cc. of dilute sulfuric acid (exactly 10 per cent by volume). When action is complete, dilute to 100 cc. with boiling water. Add sodium bicarbonate solution (80 grams per liter) from a buret and with gentle agitation until a permanent precipitate is formed (approximately 36 cc.) and then 4 cc. more. Again cover the flask, boil 1 minute, allow the precipitate to settle, and filter through a rapid filter, finally washing four or five times with boiling water. The filtrate contains all but traces of the manganese and will become cloudy in the funnel stem and receiving vessel, owing to oxidation and hydrolysis of the iron. This is to be expected. If the precipitation and filtration have been properly performed, there will be no more precipitate than can be conveniently handled on a 9-cm. paper. The manganese retained by the precipitate usually represents no more than 0.005 per cent. In umpire analyses or standardization this can easily be separated from chromium and vanadium and recovered as follows: Transfer the precipitate to a beaker, dissolve it in aqua regia, evaporate with sulfuric acid until fumes escape, cool, dilute, add sodium peroxide in excess, boil, filter, and wash the precipitate with hot water. Dissolve the precipitate of iron and manganese in warm, dilute 1:1 nitric acid, with the aid of a few drops of sulfurous acid if necessary, and add the solution to the original filtrate.

Remove the paper and precipitate from the funnel, and dissolve any coating in the funnel and stem in 25 cc. of warm, dilute 1:1 nitric acid, catching the solution in a small beaker. Heat the original filtrate to boiling and cautiously oxidize the iron with the 25-cc. portion of nitric acid used above. Evaporate the solution to about 25 cc., cool to 15° C., and add 1 to 2 grams of sodium bismuthate. Agitate thoroughly for half a minute, let stand for 1 to 2 minutes, add 50 cc. of 3 per cent nitric acid, and filter through asbestos. Wash with 3 per cent nitric acid

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[3] Kelley, Spencer, Illingsworth, and Gray, THIS JOURNAL, **10**, 19 (1918).

[4] "Methods of the Chemists of the U. S. Steel Corporation," **1921**, p. 25; *Proc. Am. Soc. Testing Materials*, **22**, I, 588 (1922).

[5] A word of caution in regard to the persulfate-arsenite method is here needed in that some texts call for standardization of the arsenite solution by titration against measured and acidified portions of a standard permanganate solution. This method gives titers which are too high. The correct procedure lies in first *reducing*, with sulfurous acid, the measured portion of the standard permanganate solution, and then oxidizing and titrating under the conditions that obtain in the method. As an illustration, the manganese titer of an arsenite solution was indicated as 0.000872 by the first method and as 0.000817 by the correct procedure. With another solution the titers obtained were 0.000230 and 0.000219, respectively. In the bismuthate-arsenite method the arsenite solution can be standardized directly against a standard permanganate solution.

[6] *Chem. Met. Eng.*, **20**, 523 (1919); "Chemical Analysis of Special Steels, etc.," 3rd ed., p. 362, John Wiley & Sons, Inc.

[7] *Reprint* **161** from *Bur. Standards, Bull.* I, No. **3**; THIS JOURNAL, **3**, 476 (1911); Blair, "Chemical Analysis of Iron and Steel," 8th ed., p. 199, Lippincott & Co.

[8] *Ann. Chem. Pharm.*, **198**, 318 (1879).

[9] This method originated with L. F. Witmer at the Bureau of Standards, and has recently appeared in *Proc. Am. Soc. Testing Materials*, **22**, I, 606 (1922). Sodium carbonate is used as the precipitant in a modification of this method, described in the "Methods of the Chemists of the U. S. Steel Corporation," **1921**, p. 23.

until the washings run through colorless. Add 3 cc. of sirupy phosphoric acid, and titrate as usual with approximately 0.03 *N* ferrous sulfate and 0.03 *N* potassium permanganate which has been standardized against sodium oxalate.

The simplicity and accuracy of this procedure is demonstrated by the results obtained by a bureau analyst in his first four analyses by it. For Sample 30*b* (0.499 per cent manganese) he obtained 0.491 and 0.492 without recovery of any manganese in the bicarbonate precipitate. In Sample 30*a* the values 0.815 and 0.816 were found. In the last run the bicarbonate precipitate was analyzed and 0.005 per cent of manganese was recovered, which gave a total of 0.821 as against the value 0.822 obtained by one of the writers in the standardization of this steel.

The following results reported for renewal No. 30*b* (average value 0.499 per cent manganese) indicate the performance of different methods for manganese—bismuthate method ($FeSO_4$-$KMnO_4$ titration) after removal of chromium and vanadium as described above: 0.500, 0.504, 0.501, 0.505, 0.50, 0.496, 0.51, 0.496, 0.494 (0.483, 0.469, 0.501); bismuthate-arsenite method: 0.502, 0.488; persulfate-arsenite method: 0.51, 0.49, 0.494, 0.50; Ford-Williams method: 0.511, 0.496; Kelley's electrometric titration method: 0.505; Johnson's PbO_2-arsenite method: 0.492. In careful analyses of steels containing not more than 2 per cent of manganese, an accuracy to ±0.01 manganese can be easily obtained; in routine analyses an accuracy to ±0.03 per cent is not difficult.

Phosphorus

The determination of phosphorus in chrome-vanadium steel is complicated by vanadium, which, when in the quinquivalent state, seriously retards the complete precipitation of the phosphomolybdate and contaminates the precipitate which is formed. Fortunately, the remedy is simple, as vanadium can be easily reduced to the quadrivalent condition in which it retards the precipitation of phosphorus much less and does not contaminate the precipitate if the precipitation is carried out at 15° to 25° C.[10] After these simple modifications the analysis is finished as in plain carbon steel; final weighing as magnesium pyrophosphate is the only suitable method for standardization purposes and the alkalimetric method meets all requirements as a routine method.[11] The following precautions are emphasized:

1—After the solution of the steel has been prepared as in plain carbon steel methods, it must be cooled to 15° to 25° C. and the vanadium reduced by the addition of a solution of ferrous sulfate and a few drops of sulfurous acid.

2—The precipitation of the phosphomolybdate must take place at 15° to 25° C., and at least 30 minutes must be allowed for complete precipitation.

3—In gravimetric determinations as magnesium pyrophosphate, it is desirable to use double the amount of molybdate reagent usually employed and to precipitate for a longer period, usually overnight. When the phosphomolybdate is dissolved in ammonia, small amounts of insoluble ferric phosphate may be left on the filter; therefore the paper should be finally washed with a little warm, dilute hydrochloric acid. Arsenic must be eliminated before the final precipitation with magnesia mixture[12] and ammonium citrate must be present during this precipitation, in order to prevent contamination of the precipitate by iron, chromium, or vanadium.

4—In volumetric determinations by the alkalimetric method, it is desirable to standardize the alkali solution against chrome-vanadium steel of known phosphorus content. The use of a phosphorus titer based on standardization by means of the bureau's standard benzoic acid and the use of a 23 : 1 ratio gave excellent results with Sample 30*b*.

The following results reported for renewal No. 30*b* (average 0.024 per cent phosphorus) indicate the performance of the different methods for phosphorus—alkali molybdate method with preliminary reduction of vanadium: 0.024, 0.024 (0.022, 0.024), 0.023 (0.021, 0.024), (0.022, 0.026), 0.026 (0.021, 0.023); gravimetric method (weighed as magnesium pyrophosphate after elimination of arsenic): 0.024, 0.024, 0.026. In umpire analyses of steels containing not more than 0.15 per cent of phosphorus an accuracy to ±0.002 per cent should be obtained by weighing as magnesium pyrophosphate, and ±0.003 per cent by volumetric or other gravimetric methods. In routine analyses an accuracy to ±0.005 per cent is easily achieved.

Sulfur

The accurate determination of sulfur in chrome-vanadium steel must be made gravimetrically, as with plain carbon steel, by precipitation as barium sulfate after solution of the steel in nitric acid (specific gravity, 1.42), repeated evaporation with hydrochloric acid, and reduction of the iron to the bivalent state. Very satisfactory rapid determinations of sulfur are possible by the evolution method.[13] The following notes are worthy of mention:

1—The precipitation of barium sulfate should be carried out in solutions containing not more than 1 to 2 per cent by volume of hydrochloric acid, and having the iron preferably in the ferrous condition. Higher acidity or the presence of ferric iron causes low results; errors due to the latter usually correspond to 0.001 to 0.002 per cent of sulfur.

2—The washing of barium sulfate precipitates obtained in steel analyses causes losses of the order of 0.001 to 0.003 per cent of sulfur. These can be eliminated by working over the washings.

3—Meineke's method[14] gave excellent results in the analysis of Sample 30*a*. The method now used differs somewhat from that described in the original article. It consists in dissolving the steel in copper-potassium chloride solution, filtering to separate the carbonaceous matter which contains the sulfur, destroying the carbon and oxidizing the sulfur by treatment with concentrated nitric acid saturated with bromine, eliminating the nitric acid by the addition of a little sodium carbonate followed by evaporations with hydrochloric acid, and finally precipitating with barium chloride in a solution containing 1 per cent by volume of hydrochloric acid.

4—Results by the evolution method with attack by dilute hydrochloric acid (1 : 1) and the use of an empirical titer obtained by titration of similar standard steel were excellent. The use of the theoretical sulfur titer of the iodine or iodate solution obtained from the Bureau of Standards standard sodium oxalate through permanganate and thiosulfate solutions, gave slightly low values on Sample 30*b* in the hands of the coöperating analysts (0.029 instead of 0.032 per cent sulfur). The bureau chemists, on the other hand, obtained excellent results (0.031 per cent as compared with the gravimetric value 0.032 per cent sulfur).

First analyses for sulfur in No. 30*b* (average value 0.032 per cent sulfur) varied from 0.029 to 0.033 in gravimetric analyses and from 0.027 to 0.033 in analyses by the evolution method. The final analyses varied from 0.030 to 0.033 and from 0.027 to 0.032, respectively. For steels containing no more than 0.15 per cent sulfur, umpire analyses by the gravimetric method should not be in error by more than ±0.002 per cent. In routine analyses an accuracy to ±0.005 per cent is easily obtained.

Silicon

The determination of silicon in chrome-vanadium steel is no more difficult than in plain carbon steel.[13] The following notes are worthy of mention:

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[10] Cain and Tucker, *Bur. Standards., Tech. Paper* **24**; THIS JOURNAL, **5**, 647 (1913).

[11] For detailed descriptions of these methods consult the references given under carbon, and also Lundell and Hoffman, THIS JOURNAL **15**, 44 (1923).

[12] Steels which contain as much arsenic as phosphorus are not uncommon; some low-phosphorus steels contain several times as much arsenic as phosphorus.

[13] See references cited under carbon.

[14] *Z. angew. Chem.*, **1**, 376 (1888).

1—With this material the Swedish method[15]—solution in sulfuric acid, evaporation until copious fumes appear, solution of soluble salts in water, and filtration—gave accurate results and less trouble than other methods.

2—In any method the period of digestion with acid following dehydration of the silica and preliminary to filtration should be as short as possible lest silica be dissolved.

3—Treatment of the ignited and weighed silica with sulfuric and hydrofluoric acids is absolutely necessary in careful analyses.

First analyses for silicon in No. 30*b* (average value 0.212 per cent silicon) varied from 0.194 to 0.22 and the final analyses from 0.204 to 0.22. For steels containing less than 0.1 per cent silicon, umpire analyses should be accurate to ±0.005 per cent; for steels containing from 0.1 to 0.3 per cent of silicon, an accuracy to ±0.01 per cent is easily attained. In routine analyses an accuracy to ±0.01 per cent and ±0.02 per cent, respectively, should be obtained.

CHROMIUM

Practically all methods for the determination of chromium in chrome-vanadium steel depend upon the oxidation of chromium to chromate and subsequent measured reduction.[16] Various oxidants are recommended, such as persulfate,[17] permanganate,[18] chlorate,[19] lead dioxide,[20] and fusion of the ammonia precipitate with sodium peroxide,[21] or carbonate and niter[22] after a preliminary separation of most of the iron.

Ferrous sulfate is universally used as the reducing medium, and it is generally added in a measured excess which is determined by final titration with permanganate; in this way vanadium and chromium are at first both reduced, but vanadium and the excess of ferrous sulfate are alone afterwards oxidized by the permanganate. The electrometric method is an exception. Here the back titration is with dichromate and finally ferrous sulfate, and therefore chromium must be obtained by subtracting vanadium as determined separately.

In all methods except the electrometric the end point causes the most concern; this is due chiefly to the color of the reduced chromium salt (also iron in the absence of phosphoric acid) and to the slowness with which the reduced vanadium is oxidized in the cool solution which is used. Other troubles are occasioned by the presence of difficultly soluble chromium carbides, by the question of complete oxidation of the chromium, and by the necessity of completely destroying all oxidants, such as permanganic acid, chlorine, and excess persulfate, before the titration.[23] In spite of these limitations most excellent determinations are possible. The following method is given because (1) it is rapid and has proved accurate in the analysis of such steels as have been tested, (2) it permits of subsequent easy determination of vanadium in the titrated solution, and (3) the circulation of the publications in which it appears[24] is limited.

PERSULFATE OXIDATION METHOD—Transfer 2.000 grams of the sample to a 600-cc. beaker and add 60 cc. of sulfuric-phosphoric acid mixture [H_2SO_4 (1 : 1) 320 cc., H_3PO_4 (sirupy) 80 cc., H_2O 600 cc.]. Heat until all action ceases, add 10 cc. of nitric acid (specific gravity, 1.20), and boil until all carbides are dissolved and oxides of nitrogen are expelled. Add silver nitrate solution (2.5 per cent) in amount equal to 0.3 gram of salt for each 1.5 per cent of chromium present. Dilute to 300 cc. with boiling water, heat nearly to boiling, and add 8 cc. of ammonium persulfate solution (15 per cent). (The purity of the persulfate should be determined as some *reagents* do not contain 25 per cent of the reagent as against 95 per cent, which is the proper strength.) If the permanganate color does not develop, add more persulfate. When the color has developed, boil the solution for 1 to 2 minutes and then add 5 cc. of sodium chloride solution (5 per cent). Continue the boiling until the pink color has just disappeared and then boil for 5 minutes longer. If the permanganate color is not destroyed by 10 minutes' boiling, or if a precipitate of manganese oxide separates, add 1 to 5 cc. of dilute 1 : 3 hydrochloric acid, and continue the boiling of the solution as above. The total period of boiling after the addition of persulfate should not be less than 15 minutes; 30 minutes will do no harm.

Cool the solution, dilute to approximately 400 cc., and titrate for chromium as follows: Add a measured excess of standard ferrous sulfate solution (50 cc. for less than 1.5 per cent of chromium, 100 cc. for 1.5 to 3 per cent chromium, etc.) and then titrate with an approximately 0.03 *N* standard potassium permanganate solution until an end point is obtained which is permanent upon continued stirring for 1 minute. The titration must be corrected for dilution effect and color interference. In colored solutions the correction can be made (1) empirically as in the U. S. Steel Corporation methods,[25] (2) by titration of the same volume of ferrous sulfate in a solution of like volume and acidity and containing the same amount of the coloring elements in their final valency, or (3) in the final titrated solution. The last is the most convenient and satisfactory in occasional analyses, and may be performed by destroying the slight excess of permanganate which is present by boiling for 10 minutes, cooling to room temperature, and then titrating with the permanganate solution to the same end point that was taken before. The volume of permanganate here required—about 0.2 cc. 0.03 *N* solution for a 1 per cent chrome-vanadium steel such as 30*b*—is to be subtracted from the result of the first titration. The difference is then a true oxidizing equivalent of the excess of ferrous sulfate employed, and the percentage of chromium may be calculated in the usual manner from a standardization based on sodium oxalate. The final solution should be preserved for the determination of vanadium as below. Tungsten, nickel, cobalt, molybdenum, arsenic, and uranium do not interfere in the foregoing method. With tungsten steel the titration is peculiar in that the solution is dark at first, owing to some tungsten-quadrivalent vanadium compound, and then clears considerably as the end point is approached.

That the method is accurate and not troublesome is indicated by the following analyses by a bureau analyst who had never used the method before: Sample 30*b*, 1.02 and 1.02 per cent chromium as compared with the recommended value 1.03; Sample 30*a*, 1.02 and 1.02 per cent chromium as compared with the recommended value 1.02; Sample 50 (tungsten 17.56 per cent, chromium 3.61 per cent, vanadium 0.756 per cent), 3.56 and 3.69 as compared with 3.61 per cent. With Sample 50 it was found advisable to use only 0.5 gram of sample on account of the peculiar end point.

The following results reported for renewal No. 30*b* (average value 1.03 per cent chromium) indicate the performance of the different modifications of the oxidation procedure: permanganate oxidation (*a*) Johnson's method, 1.01, (*b*) Barba's method,[26] 1.05; bismuthate oxidation, 1.01; chlorate oxidation, 1.02, 1.00; fusion with peroxide, 1.03;[27] persulfate oxidation methods (*a*) unclassified, 1.00, 1.04, 1.02, (*b*) with

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[15] *Proc. Am. Soc. Testing Materials*, **22**, I, 597 (1922).

[16] An exception to this procedure is that employed in an unpublished method developed by L. F. Witmer at this bureau; in this method chromium is reduced to the divalent state in a Jones reductor and afterwards oxidized to the trivalent condition by standard permanganate.

[17] "Methods of Chemists of U. S. Steel Corporation," **1921**, p. 43; Johnson, *loc. cit.*, p. 28; Kelley and Conant, THIS JOURNAL, **8**, 719 (1916); *Proc. Am. Soc. Testing Materials*, **22**, I, 609 (1922).

[18] Johnson, *loc. cit.*, pp. 5, 21; Blair, *loc. cit.*, p. 187. Ibbotson, "The Chemical Analyses of Steel Works Materials," p. 110, Longmans, Green & Co. "Methods of Chemists of U. S. Steel Corporation," **1921**, p. 46.

[19] Am. Soc. Testing Materials, Standards, **1921**, pp. 281, 294.

[20] Blair, *loc. cit.*, p. 188.

[21] Blair, *loc cit.*, p. 184.

[22] Am. Soc. Testing Materials, Standards, **1921**, pp. 271, 279, 292.

[23] Kelley and Conant, *loc. cit.*, admirably sum up the pitfalls in this process.

[24] "Methods of the Chemists of the U. S. Steel Corporation," **1921**, p. 43; *Proc. Am. Soc. Testing Materials*, **22**, I, 609 (1922).

[25] "Methods of Chemists of U. S. Steel Corporation," **1921**, p. 44.

[26] Blair, *loc. cit.*, p. 187.

[27] At this bureau it has been found practically impossible to get chromium completely oxidized to chromate by fusion, water extraction, and filtration through asbestos; consequently the water extract is always acidified with sulfuric acid, treated with nitric acid, and oxidized with silver nitrate and persulfate before the final titration.

final electrometric titration, 1.01, 1.02, (c) by the method described above, 1.03, 1.04, 1.02, 1.03 (1.00, 1.01), 1.01, 1.02, 1.04, 1.05, 1.02.

In careful determinations of chromium an accuracy to ±0.01 per cent should be obtained with steels containing not more than 1 per cent of chromium, ±0.03 per cent for steels containing 5 per cent, and ±0.10 for steels containing 20 per cent. In the same steels the accuracy obtained in routine determinations should approach ±0.02, ±0.06, and ±0.15 per cent, respectively.

VANADIUM

Aside from the colorimetric method,[28] which is chiefly used under favorable conditions for works control, the principally used methods for the determination of vanadium are volumetric and are based on its change from the quadrivalent to the quinquivalent condition, or vice versa. The reduction of vanadium is easily performed in solutions at room temperature; its oxidation, on the other hand, does not proceed as easily and is best performed at 60° to 80° C. With acid solutions containing vanadium alone the foregoing methods are quite exact, as there is no color interference and the solution can be heated if desired. Unfortunately, unless previous separations are performed, the solutions which are encountered in steel analysis contain salts of iron and often salts of such elements as chromium and nickel, which either obscure the end point or will not permit heating of the solution. These drawbacks are not fatal in routine analyses; they are, however, troublesome in accurate analyses, especially where the amount of vanadium is low and sometimes corresponds to less of the standard solution than the blank correction.

Chief among the methods depending on measured reduction are Johnson's[29] and Kelley's.[30] The former is widely employed and depends on the reduction of vanadium by means of a standard solution of ferrous sulfate and the use of ferricyanide as an internal indicator. The chief difficulty with this method lies in judging the end point, which is complicated by the normal color of the solution and by a slight interaction between the reduced vanadium and ferricyanide which yields ferrocyanide and a consequent blue color. Aside from this, in the case of renewal No. 30*b*, an additional difficulty[31] is introduced by the abnormal amount of copper (0.13 per cent) which reacts with the indicator. Kelley's method is an electrometric titration method in which the vanadium is oxidized by nitric acid and then reduced by ferrous sulfate with back titration with dichromate and ferrous sulfate. As the oxidation of vanadium by nitric acid is not quite complete, a correction factor is employed.[32] The method yields excellent results and is free from color interference; its chief drawback lies in the apparatus required.

Campagne's method[33] is perhaps the most widely known of the measured oxidation type. Here an ether separation removes most of the iron and evaporations with hydrochloric acid serve to reduce the vanadium, which is then titrated with permanganate after evaporation with sulfuric acid to remove hydrochloric acid. In this method positive errors may be occasioned by iron reduced during the ether extraction, by organic matter from the ether, by uncorrected end points, and by titration in a hot solution in the presence of chromium. Negative errors are occasioned by the slight solubility of vanadium in ether, by incomplete reduction with hydrochloric acid, and by slight oxidation due to prolonged heating with sulfuric acid. The method of the chemists of the U. S. Steel Corporation[34] is less widely known, and is given below because it has not been described in the journals and in the writers' hands has proved to be rapid and as accurate as any of those described above, except Kelley's. The method is based on the behavior of ammonium persulfate in a *cold* acid solution containing *no* silver nitrate. Under these conditions it oxidizes ferrous sulfate but does not react with quadrivalent vanadium, permanganate, bivalent manganese, or trivalent chromium. Therefore, it is possible to reduce vanadium by an excess of ferrous sulfate, to destroy the excess with persulfate, and then to titrate the reduced vanadium with permanganate.

METHOD I—(For the Routine Determination of Vanadium) See the "Determination of Chromium" above. Use the solution employed for the determination of chromium (as given above), and add 10 cc. of approximately 0.03 *N* ferrous sulfate solution if vanadium is under 0.80 per cent, 20 cc. if the vanadium content is higher, etc. Stir the solution thoroughly, add 8 cc. of ammonium persulfate solution (15 per cent solution of the 95 per cent salt) and stir for 1 minute. Titrate with approximately 0.03 *N* permanganate solution to a definite pink color which does not fade upon continued stirring for 1 minute. As in the determination of chromium, an excess of permanganate is consumed in order to overcome the dilution effect and the color interference. If this excess was actually determined after the chromium titration, the same correction should be subtracted here. If an empirical correction is made in accordance with the U. S. Steel Corporation method, a blank must be deducted equal to 0.02 per cent plus 1.8 per cent of the chromium present. It should be noted that the effect of the blank is here reversed; it lowers the percentage of vanadium but raises the percentage of chromium. Chromium, nickel, cobalt, molybdenum, arsenic, and uranium do not interfere in the foregoing method. Tungsten does interfere and must be separated in a new sample before the method is used. The performance of this method is indicated by the following results obtained by a bureau analyst in his first four analyses by it: 0.216 and 0.216 as against the recommended value 0.215 per cent vanadium in Sample 30*b*, and 0.214 and 0.216 compared with the recommended value 0.21 per cent vanadium in Sample 30*a*.

As the foregoing methods are subject to various limitations which cast the results in doubt—often very much so in the hands of novices or where only a few hundredths of one per cent of vanadium are in question—the following method is also presented. In this method, which is a modification of that described by Cain,[35] most of the iron is eliminated by a bicarbonate precipitation as described under manganese, and the remainder of the iron, together with chromium and copper, is completely removed by dissolving the precipitate and electrolyzing with a mercury cathode in a dilute sulfuric acid solution. Cobalt and nickel are also quantitatively removed, while phosphorus, arsenic, molybdenum, manganese, aluminium, titanium, zirconium, and uranium remain with vanadium in the electrolyte. The vanadium in the electrolyte is then reduced by sulfur dioxide, titrated with permanganate, and the final solution qualitatively tested for vanadium if desired. This method is not subject to the usual interfering elements, and is well suited for purposes of primary standardization and for the isolation and identification of vanadium.

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[28] "Methods of the Chemists of the U. S. Steel Corporation," **1921**, p. 50.

[29] "Chemical Analysis of Special Steels, etc.," 3d ed., p. 6, J. Wiley & Sons, Inc.

[30] THIS JOURNAL, **11**, 632 (1919).

[31] Private communication from C. M. Johnson.

[32] Willard and Fenwick in a recently published method [*J. Am. Chem. Soc.*, **45**, 84 (1923)] use a polarized bimetallic electrode system instead of the usual monometallic combination [*J. Am. Chem. Soc.*, **44**, 2516 (1922)], and titrate vanadic acid directly with ferrous sulfate because of the more sensitive end point. Complete oxidation to vanadic acid is obtained by preliminary boiling with nitric acid followed by treatment with a slight excess of potassium permanganate, and any chromate formed is destroyed by boiling with sodium perborate in acetic acid solution.

[33] *Compt. rend.*, **137**, 570 (1903).

[34] "Methods of the Chemists of the U. S. Steel Corporation," **1921**, p. 47; *Proc. Am. Soc. Testing Materials*, **22**, I, 617 (1922).

[35] *Bur. Standards, Bull.* **7**, 377 (1911); THIS JOURNAL, **3**, 476 (1911); Blair, *loc. cit.*, p. 199.

Method II—(For the Accurate Determination of Vanadium) Dissolve 2.000 grams of the sample contained in a 200-cc. Erlenmeyer flask, in 30 cc. of dilute sulfuric acid (10 per cent by volume). If the steel contains less than 0.1 per cent vanadium, use a larger sample and correspondingly more acid. When action is complete, dilute to 100 cc. with boiling water, heat to boiling, and proceed with a sodium bicarbonate precipitation as in the determination of manganese described above.

Place the paper and sodium bicarbonate precipitate in the original flask, add 20 cc. of nitric acid (specific gravity, 1.42), shake until the paper is broken up, and then add 5 cc. of sulfuric acid (specific gravity, 1.84). Heat over a free flame until fumes of sulfuric acid are given off, cool, and then add more nitric acid and repeat the heating if the organic matter has not been destroyed. Finally, cool, wash down the sides of the flask, and evaporate again until fumes of sulfuric acid appear and until it is certain that all the nitric acid has been expelled. Cool, dilute to 40 cc.,[36] neutralize the solution with ammonia, and then add 1 per cent by volume of sulfuric acid in excess. Transfer the weakly acid solution to the electrolyzing apparatus, rinsing the flask with small portions of water, and keeping the total volume of the solution down to 70 cc. The electrolysis may be performed with a mercury cathode in (1) the special modified separatory funnel described and pictured by Cain[35] and also by Blair;[37] (2) in a small beaker with sealed in platinum wire as described by Smith,[38] or (3) in an ordinary beaker with the cathode lead enclosed in a glass tube extending into the mercury. In any case the cathode lead should be imbedded in about 200 grams of mercury, and the solution electrolyzed (preferably with a stirring arrangement) using a current of 5 to 6 amperes at 6 to 7 volts. Continue the electrolysis until iron is removed as indicated by a ferricyanide test on a small drop of the electrolyte. This will ordinarily require 15 to 20 minutes if the electrolyte is stirred. When iron is absent, remove the electrolyte and wash the mercury two or three times with 25 to 30 cc. of water while the current is continued. If the electrolyte is not absolutely free from iron, the electrolysis must be continued until it is. Arsenic is the only element to be feared. The small amounts of arsenic (up to 0.02 per cent) usually present in steel may be ignored except in the most accurate work. In precise work or where large amounts of arsenic are present, the properly acidified electrolyte must be treated with hydrogen sulfide, the solution filtered, and every trace of hydrogen sulfide expelled from the filtrate before the preliminary oxidation with permanganate as above. If all hydrogen sulfide is not expelled, this oxidation gives rise to sulfur which later reacts with sulfur dioxide to yield oxidizable products which cause high and erratic values for vanadium. Add 2 to 3 cc. of dilute sulfuric acid (1 : 1), heat to 70° to 80° C., and add permanganate solution until a strong pink color appears. Pass sulfur dioxide into the boiling solution for a few minutes, or until the vanadium is reduced to the quadrivalent condition, and then a rapid stream of carbon dioxide free from oxygen until the solution is free from sulfur dioxide, as shown by bubbling the stream through a feebly acidified dilute solution of permanganate. The direct use of a solution of sulfur dioxide or of any alkali sulfite is inadmissible unless these have been freshly prepared, for after a lapse of time they contain other oxidizable bodies than sulfurous acid or sulfite. Sulfur dioxide is most conveniently used from a cylinder of the liquefied gas, or it may be obtained as wanted by heating a flask containing a solution of sulfur dioxide, or of a sulfite to which sulfuric acid is added.[39] Sulfur dioxide must, of course, be entirely removed before the succeeding titration. Cool the solution to 60° to 80° C. and titrate with 0.03 *N* potassium permanganate solution which has been standardized against sodium oxalate. Repeat the reduction and the titration until concordant results are obtained. The titration should be corrected by a blank determination (usually amounting to about 0.10 cc.) on a solution of like volume and acidity. The final solution may be evaporated to small volume and qualitatively tested for vanadium with hydrogen peroxide in acid solution, or with hydrogen sulfide in ammoniacal solution.

This method is not as troublesome as might appear at first sight, and is quite rapid if such facilities as an electrolyzing apparatus and cylinders of sulfur dioxide and carbon dioxide are at hand. When the mercury has become saturated with iron and chromium, a fair degree of purification can be attained in a few minutes by shaking in a separatory funnel with concentrated hydrochloric acid.[40]

The following results reported for renewal No. 30*b* (recommended value = 0.215 per cent vanadium) indicate the performance of the different methods: colorimetric method[28] (0.18, 0.21), 0.19; Johnson's method,[41] 0.22,[42] 0.20; Garratt's modification of Johnson's method,[43] 0.22; Kelley's electrometric titration method, 0.22, 0.22; Cain and Hostetter's method,[44] (0.26, 0.20), 0.20; Campagne's method,[33] 0.18, 0.19, 0.20; Blair's method[45] (final procedure as in Campagne's method), 0.22; Method I, 0.21, 0.21, 0.18, 0.20, 0.21, 0.20; Method II, 0.22, 0.21, (0.16, 0.21), 0.20.

In careful analyses an accuracy to ±0.01 per cent can be easily attained with steels containing 1 per cent of vanadium and ±0.02 per cent with steels containing 2 per cent. In routine analyses an accuracy to ±0.02 per cent in low vanadium steel and ±0.04 for 1 per cent, and ±0.06 for 2 per cent vanadium steels is to be expected.

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[36] Tungstic acid retains vanadium (about 0.01 mg. for each per cent of tungsten in the steel [Kelley, Wiley, Bohn, and Wright, This Journal, 11, 633 (1919)]. Consequently, if any appreciable amount is present at this stage, the solution must be filtered and the washed residue dissolved in an excess of ammonia. Vanadium is then separated from tungsten by the addition of 1 g. of alum, precipitation by a slight excess of ammonia, filtration and washing. The precipitate is dissolved in hot dilute hydrochloric acid, heated with 1 to 2 cc. of sulfuric acid till fumes appear, and the solution added to the original filtrate.

[37] *Loc. cit.*, p. 200.

[38] "Electro-analysis," 5th ed., p. 62, P. Blakiston's Son & Co.

[39] W. F. Hillebrand, *U. S. Geol. Surv., Bull.* **700**, 186.

[40] For more complete purification, see J. H. Hildebrand, *J. Am. Chem. Soc.*, **31**, 933 (1909).

[41] *Loc. cit.*

[42] With preliminary removal of copper.

[43] Garratt, This Journal, **4**, 256 (1912).

[44] Cain and Hostetter, *Ibid.*, **4**, 250 (1912).

[45] Blair, *loc. cit.*, p. 209.

Wearing Qualities of Shoe Leathers

Wearers of shoes need definite information on the wearing quality of leather to enable them to buy shoes economically; tanners need such knowledge to enable them to make high-grade leather and to use their raw material to the best advantage and at the lowest cost. To supply this information, the Bureau of Chemistry in 1919 began a series of experiments at various army training camps, which furnish the basis for a bulletin recently issued by the Department of Agriculture.

It was evident from these experiments that shoe uppers made from the better portions of cow-grain leathers of good quality will outwear two or more soles. Fiber soles of the kinds used were not suitable for the conditions of wear, owing principally to the fact that as soon as the soles had worn down through the stitches they frequently ripped and broke off. Imperfections, such as ripping, bulging, chipping, and breaking, were numerous in the fiber soles.

Disregarding the possibility of misfitting, a full double sole and double shank of heavy leather seems to be responsible for the wasteful excessive toe wear, as such a shoe bends but little and the weight of the body is concentrated at the extreme end of the sole, instead of being distributed over a greater area at the ball.

The serviceability of various tannages, based on a standard thickness of 9 irons, was found to be as follows: oak bark, 78 days; hemlock bark, 79 days; chestnut wood extract, 80 days; belting, 85.5 days; waxed chrome, 102 days; unwaxed chrome, 126 days; and fiber soles, 122 days. Among the outstanding indications of the experiments are the superior pliability of retanned-chrome and chrome-tanned upper leathers, certain objectionable features of fiber soles and the long wear of those that did not develop such features, the increased serviceability of rolled sole leathers, and the strikingly longer wear of chrome-tanned sole leathers, especially of the unwaxed chrome-tanned leather.

SUGGESTIONS TO AUTHORS

The booklet "Suggestions to Authors," which we recently announced was in preparation, is now ready for distribution, and copies will be mailed to those who will send a request therefor to the editor's office.

Coöperation of authors in following these suggestions will be greatly appreciated in the editorial office, and by lessening ambiguity and thus making possible more prompt publication will help to bring about better satisfaction to all concerned.

The Freezing Point-Solubility Diagram of the System Tetryl-Picric Acid[1]

By C. A. Taylor and William H. Rinkenbach

Bureau of Mines, Pittsburgh, Pa.

THE freezing point curves of the binary systems of TNT-tetryl[2] and TNT-picric acid[3] have previously been determined by the writers, and the freezing point curve of tetryl-picric acid, as herein discussed, completes the series.

The method, apparatus used, and the purification of the materials employed in this work have been described in detail in the articles mentioned. The tetryl had a setting point of 128.72° C., and that of the picric acid was 121.9° C. Each was melted and cooled before being used.

Considerable difficulty was encountered in obtaining accurate check results on the same mixture in the course of the work on mixtures of tetryl and picric acid. This difficulty was found to be due to a tendency on the part of these mixtures to supercool to a remarkable degree. For example, a melt containing 50 per cent of each component cooled to room temperature without the formation of a solid phase. The cold, extremely viscous liquid so obtained remained in this state for about 10 days, although the forcing of crystallization by means of "seeding" was attempted, and it then solidified very slowly. Another melt that was constantly agitated supercooled to room temperature, began to solidify slowly after 2 hours, and caused a rise in temperature of only 2 degrees.

Molecular Percentage of				Cooling Points Found Average ° C.	Melting Point ° C.
Tetryl	Picric Acid	Tetryl	Picric Acid		
0.00	100.00	0.00	100.00	121.8	....
15.00	85.00	12.34	87.66	111.75	....
30.00	70.00	25.48	74.52	99.9	....
40.00	60.00	34.72	65.28	90.0	....
45.00	55.00	39.50	60.50	84.8	85.6
47.50	52.50	41.92	58.08	81.05	....
50.00	50.00	44.38	55.62	76.65	85.5
52.50	47.50	46.86	53.14	72.2	85.5
55.00	45.00	49.43	50.57	....	85.5
58.00	42.00	52.42	47.58	77.3	....
60.00	40.00	54.48	45.52	81.0	....
62.00	38.00	56.55	43.45	84.2	84.6
65.00	35.00	59.71	40.29	90.1	....
70.00	30.00	65.05	34.95	98.3	....
77.14	22.86	72.92	27.08	108.9	....
88.12	11.88	85.14	14.86	120.2	....
90.00	10.00	87.78	12.22	121.75	....
100.00	0.00	100.00	0.00	128.72	....

In addition to the use of cooling curves for the derivation of equilibrium data, it was found advisable to employ heating curves. These were obtained by gradually heating the previously cooled melt in the apparatus used for cooling curve work, the temperature of the bath being slightly higher than that necessary for the formation of a homogeneous solution. The rise in temperature of the melt was steady until the saturation temperature was reached, when there was a period during which the temperature of the melt remained constant.

The results obtained by the use of both cooling and heating curves are shown in the table and in Fig. 1.

Interpretation of Results

Inspection of the curve derived from the foregoing data shows a different type than TNT-tetryl and TNT-picric acid. Curves showing the lowering of the melting points of the pure components in the usual way are obtained except in mixtures containing 44 to 63 per cent tetryl. A melt containing 50 per cent of each component, for example, gave a cooling curve of the type shown in Fig. 2. The maximum temperature attained (*d* in Fig. 2) varied in individual cases from 75.6° to 81.9° C. When this same mixture was allowed to solidify and was then slowly heated, a curve (Fig. 3) indicating a melting point of 85.5° C. was obtained. The other mixtures within this concentration range gave similar results.

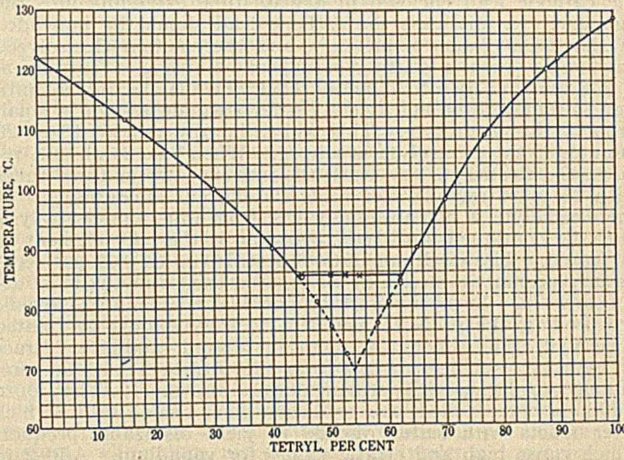

Fig. 1—Freezing Point Curve of Tetryl and Picric Acid

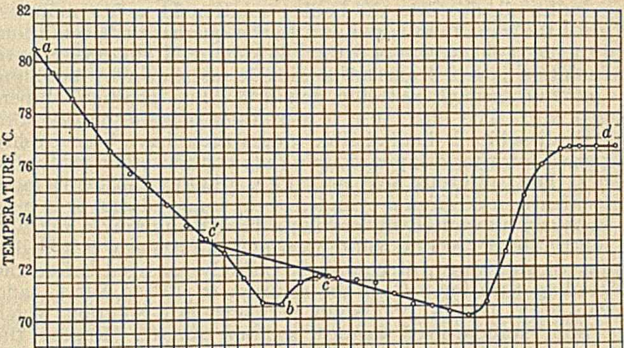

Fig. 2—Cooling Curve of Mixture of Tetryl and Picric Acid

Plotting these results (Fig. 1), we have a curve indicating the formation of a compound of the components. However, on account of the great tendency on the part of this compound to supercool, as previously shown, it was possible to complete the curve on both branches through the metastable condition.

Composition of Compound Formed

Calculation shows that the percentage composition of the simple compounds usually formed in such cases is as follows:

1 molecule tetryl : 2 molecules picric acid 38.52 per cent tetryl
1 molecule tetryl : 1 molecule picric acid 55.62 per cent tetryl
2 molecules tetryl : 1 molecule picric acid 71.47 per cent tetryl

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[1] Received May 1, 1923. Published by permission of the Director, U. S. Bureau of Mines.

[2] This Journal, **15**, 73 (1923).

[3] *Ibid.*, **15**, 795 (1923).

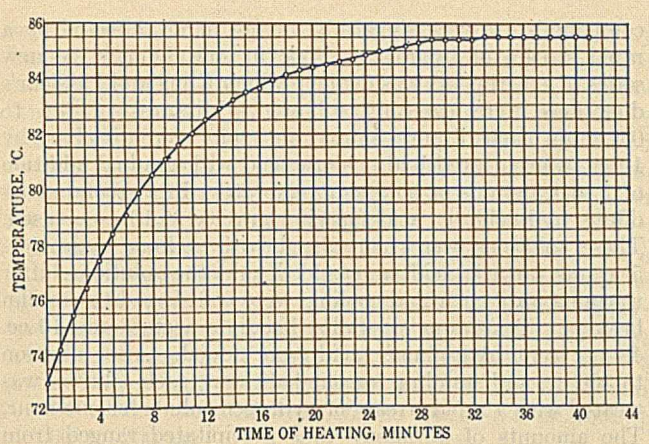

Fig. 3—Curve Showing Rise in Temperature as Mixtures of Tetryl and Picric Acid Are Heated at Uniform Rates

From this it would appear that the compound formed consists of one molecule of tetryl and one molecule of picric acid, as the others are outside the concentration range covered by the flat portion of the curve.

Melts of the pure components and various melts of these two were submitted to W. M. Myer, petrographer of the Bureau of Mines, Pittsburgh, Pa., for examination. He found that there was a third substance present in the melts, but owing to the high refractive indices of all the substances, it was not possible to make quantitative comparisons.

Application of the Data

The data can be applied to the analysis of mixtures of tetryl and picric acid in the manner described in the paper dealing with mixtures of TNT and tetryl.[2] However, it is difficult to use this method within the concentration range 44 to 63 per cent of tetryl, because of the difficulty in obtaining accurate checks and the peculiarities of this portion of the curve. The difficulty in obtaining accurate checks may be ascribed to the fact that the supercooled mixtures are rather viscous. Thick suspension of air bubbles is quickly formed when the melt is stirred, and this prevents an even rate of heat transference, so that the uneven rate of cooling under the best of conditions yields results that are not within the usual range of accuracy.

Acknowledgment

The writers wish to express their appreciation of the many helpful suggestions on the interpretation of the data given by R. E. Hall, physical chemist of the Pittsburgh Experiment Station, Bureau of Mines.

The Separation of Tin from Other Metals[1]

Including Its Determination after Precipitation by Means of Cupferron

By **N. Howell Furman**

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Kling and Lassieur have proposed the use of cupferron as a precipitant for quadrivalent tin. This method has been studied in detail, and found to be rapid, convenient, and accurate. It is especially suitable in connection with the analysis of tin-antimony alloys by the McCay method.

An alternate electrolytic method which Kling and Lassieur recommend highly has not been found to be satisfactory for the rapid determination of tin.

Attention has been called to a widespread serious misunderstanding of the conditions which are necessary for the separation of antimony from tin in dilute hydrofluoric acid solutions.

By means of established methods, together with some additional ones here described, tin may be separated from copper, lead, arsenic, antimony, bismuth, cadmium, zinc, manganese, cobalt, and nickel.

Nearly all the metallic elements which are commonly associated with tin in alloys—namely, cadmium,[2] copper, lead, bismuth,[2] arsenic, and antimony—may be separated completely from quadrivalent tin by precipitation with hydrogen sulfide in solutions which contain a moderate concentration of hydrogen fluoride (about 1 per cent by weight). In his comprehensive scheme of qualitative analysis, Noyes[3] made mention of the possible use of dilute hydrofluoric acid solutions of certain metals in quantitative analysis.

McCay has proved that the separations from tin are quantitative in the cases of antimony,[4] lead,[5] copper,[5] and arsenic.[6] His experiments prove that the separations are successful only when antimony and arsenic are present quantitatively in the trivalent, and tin in the quadrivalent state. Iron and zinc, if present, will be found in the filtrate which contains the tin. Preliminary results indicate that under the conditions recommended by McCay[5] in his scheme for the analysis of the tin-antimony alloys, no zinc is precipitated with the copper sulfide. This detail is being studied further.

McCay has proposed a simple and accurate method for the analysis of the tin-antimony alloys, which is based upon his excellent method for the separation of antimony from tin.[4,5] The only criticism of the original method of which the author is aware was directed toward the necessity of using a platinum dish to remove the hydrogen fluoride before a determination of tin could be made.

It was later shown by the author that the fluorine can be removed from the sphere of action by the addition of a large excess of boric acid to the solution. After the fluorine has thus been bound, perhaps in the little dissociated anion, BF_4^-, a complete precipitation of the tin as sulfide can be made in a glass vessel.[7] Alternately, it was pointed out that the tin can be deposited electrolytically after the addition of oxalic acid.[8] The current efficiency was extremely

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[1] Received March 23, 1923.

[2] Thus far qualitative experiments only have been made in the instances of cadmium and bismuth. See Footnote 4.

[3] *Tech. Quarterly*, **16**, 93 (1903); **17**, 214 (1904).

[4] *J. Am. Chem. Soc.*, **31**, 373 (1909).

[5] *Ibid.*, **32**, 1241 (1910).

[6] *Ibid.*, **45**, 1187 (1923).

[7] Furman, *J. Am. Chem. Soc.*, **40**, 895 (1918).

[8] The details which are described in Classen-Hall, "Quantitative Analysis by Electrolysis," 5th ed., **1913**, p. 135, John Wiley & Sons, Inc., were followed.

low, however, and the process was so time-consuming as to be impractical.

Recently, Kling and Lassieur[9] have recommended the McCay method for the separation of antimony from tin,[4] followed by the precipitation of the tin in the filtrate by means of cupferron, after the addition of a large excess of boric acid. In a subsequent communication[10] they state that the electrolytic precipitation of the tin is to be preferred to the precipitation by means of cupferron. They have found that a complete deposition of tin may be made in 20 minutes by using a current of 4 to 5 amperes and an apparatus suitable for rapid electro-analysis. (The electrode areas were not stated, nor were any experimental results given.)

Their solutions differed from those which were previously employed by the author only in having present 2.5 grams tartaric acid, 5 to 10 grams sodium acetate, and 10 cc. concentrated hydrochloric acid, in addition to the quantities of other substances normally present.

An extended series of quantitative experiments was made in which the conditions were as closely as possible those of Kling and Lassieur. Each solution contained 0.1 to 0.25 gram tin, 5 cc. 48 per cent hydrofluoric acid, 4 to 6 grams boric acid, 5 to 7 grams ammonium oxalate, 5 to 10 grams crystallized sodium acetate, and 5 to 10 cc. concentrated hydrochloric acid (specific gravity, 1.19). The tin was introduced in the form of stanni-ammonium chloride solution containing appropriate quantities of hydrochloric acid. The total volume was between 100 and 200 cc. A current strength of 4 to 5 amperes per 100 sq. cm. cathode surface at 4 to 6 volts was employed; the speed of anode rotation was 600 to 800 per minute. In no case was the tin completely deposited in one hour. The quantities not precipitated varied from 1 to 3 mg. A further electrolysis of 1 to 2 hours under the same conditions was necessary to complete the deposition. The small quantities of tin which were not precipitated in the first hour were always recovered upon continued electrolysis with cathodes freshly plated with copper; much less than 1 mg. of tin could be easily seen under these conditions.

With stationary electrodes, employing a current of 0.5 ampere per 100 sq. cm. cathode at 3 to 4 volts, other conditions as described above, complete deposition of the tin required 20 to 24 hours. In the original experiments,[7] which were made with sulfate solutions and without sodium acetate, the time required with stationary electrodes was 40 to 48 hours, other conditions being as here described. The acceleration of the deposition is undoubtedly due to the presence of both acetates and chlorides.[11] Even with these additions, the method leaves much to be desired.

Kling and Lassieur state that the cupferron precipitation of tin is most satisfactory from the standpoint of rapidity, ease of washing, and ignition of the tin to constant weight as oxide. Inasmuch as only three test analyses were given in the two papers cited, it seemed desirable to investigate the method further, especially since these results were obtained after precipitation of the antimony from a "hydrochloric acid solution of the two metals oxidized by potassium chlorate." Such a procedure makes the separation of the antimony from tin absolutely unreliable.[12]

Numerous qualitative experiments have shown conclusively that dilute hydrofluoric acid solutions of *antimonic* compounds are very sluggishly, or not at all, affected by a rapid stream of hydrogen sulfide in one hour.[13] A new series of experiments was made in which Kling and Lassieur's directions were carefully followed. Mixtures of 0.1 to 0.3 gram each of pure tin and antimony were dissolved by 10 cc. concentrated hydrochloric acid with gradual addition of 1 to 1.5 grams of potassium chlorate. In a second series dilute hydrochloric acid (specific gravity, 1.10) was used. These solutions were neutralized with sodium hydroxide, 5 grams tartaric acid were added, and the solutions, after warming until clear and cooling, were transferred to paraffin beakers. Ten grams crystallized sodium acetate and 10 cc. 48 per cent hydrofluoric acid were added. After dilution to 300 cc. and standing for one-half hour, each solution was treated with a rapid stream of hydrogen sulfide for one hour. The amounts of antimony thus precipitated ranged from 0.6 to 54 per cent of the quantities known to be present. Presumably, these figures represent the portion of the antimony which was not oxidized by the potassium chlorate.

Abundant evidence of the presence of antimony in the filtrate was always obtained upon adding an excess of boric acid, warming the solution in a glass vessel, and again saturating it with hydrogen sulfide. The presence of a large amount of antimony sulfide admixed with the tin sulfide thus precipitated was confirmed by careful qualitative work.

A similar erroneous idea of the conditions which are necessary for the separation of antimony from tin by the McCay method is to be found in the work of Ibbotson and Aitcheson.[14]

It cannot be too strongly emphasized that the antimony must be in the lower state of oxidation in order that this separation shall be complete.

Experimental

A solution of stannic tin was prepared by dissolving about 4 grams of pure tin (the tin was of known high degree of purity, having been tested in connection with previous investigations of this series[4,5]) in 40 cc. of hot concentrated sulfuric acid. The solution was diluted to a liter after the addition of enough hydrochloric acid to prevent hydrolysis. Known portions of this solution were taken for analysis. Volumes recorded are at 20° C. The tin was precipitated as metastannic acid and weighed as oxide, following the method of Rose.[15] The following values were obtained:

	Solution Taken Cc.	Tin Found Gram
	25	0.1032
	50	0.2062
	25	0.1034
	25	0.1041
Average	25	0.1034

Precipitation of Tin by Means of Cupferron—Numerous analytical uses of cupferron (nitrosophenylhydroxylamineammonium) have been proposed since this reagent was first introduced by Baudisch.[16] A compre-

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[9] *Compt. rend.*, **170**, 1112 (1920).

[10] *Ibid.*, **173**, 1081 (1921).

[11] Engels, *Ber.*, **28**, 3187 (1895).

[12] H. H. Willard has pointed out (private communication) that the accuracy of the tin results would not be affected since quinquivalent antimony is not precipitated by cupferron. This suggestion was studied experimentally and found to be correct. Kling and Lassieur give results which are correct for both antimony and tin.

[13] The author has made many qualitative experiments, dissolving 0.5 to 1.0 gram of pure potassium antimoniate in hydrofluoric acid (5 to 10 cc.). Upon dilution to 250 to 350 cc. and passage of hydrogen sulfide for one hour, a slight yellow coloration sometimes appears after the first half hour. Upon standing, the solution generally becomes clear in a few hours. With a deficiency of acid, however, more or less rapid precipitation of antimony may occur.

[14] "The Analysis of Non-Ferrous Alloys," 2nd ed., **1922**, p. 132, Longmans, Green & Co., has the following erroneous statement: "For this separation (i. e., antimony from tin) the metals should exist in the higher state of oxidation in hydrochloric acid solution.*** The solution *** is treated with an excess of tartaric acid and then neutralized with sodium hydrate. A solution of 48 per cent hydrofluoric acid is then added, and this is followed by an excess of sodium acetate. After diluting largely *** the antimony is precipitated by a current of sulfuretted hydrogen," etc. No more unsuitable conditions could well have been chosen!

[15] *Pogg. Ann.*, **102**, 164 (1861).

[16] *Chem. Ztg.*, **33**, 1298 (1909).

hensive review of these uses has recently been made by Lundell and Knowles.[17] Marvel and Kamm[18] have studied and improved the methods of preparing cupferron. Presumably, the tin precipitate with cupferron is essentially $Sn(C_6H_5N_2O_2)_4$. Auger[19] states that he has commenced a study of the complex salts of cupferron with molybdenum, tin, and cerium; hence no attempt was made to establish the composition of the precipitate.

Known portions of the tin solution were taken. In a number of cases the conditions were as nearly as possible those which would be encountered in the analysis of a copper-lead-tin-antimony alloy by the McCay method—namely, 0.1 to 0.3 gram tin, 5 cc. 48 per cent hydrofluoric acid, 4 grams boric acid, 2 to 5 cc. concentrated sulfuric acid, and 5 to 10 cc. concentrated hydrochloric acid in a total volume of 200 to 500 cc.

The cupferron was added in the form of a 10 per cent solution. The solution was filtered before using. Such a solution is stable for several weeks.[20] Upon the addition of the reagent the tin precipitate separates in a white form, which is possibly an emulsion; it rapidly assumes a curdy appearance. Upon vigorous stirring in the presence of an excess of cupferron the precipitate generally passes through a stage in which it resembles superficially plastic sulfur. Finally, it becomes compact and brittle, and may be crushed to a powder with a glass rod.[21] The whole series of transformations usually requires 30 to 45 minutes. Kling and Lassieur commence the filtration when the curdy state has been reached. In this study excellent results were obtained with the brittle precipitate, the filtration being very rapid. The precipitate ordinarily has a yellowish appearance when it has become brittle and compact. There is a very noticeable clearing up of the solution when precipitation is complete. A liberal excess of cupferron is desirable.

The precipitate was washed with cold water. Precipitation and washing may easily be completed in less than an hour. After drying in a weighed crucible, the organic matter was expelled by gentle ignition. The stannic oxide was brought to constant weight in the usual manner. If the quantity of tin is larger than 0.1 to 0.3 gram, it becomes increasingly difficult to remove carbon. By breaking up the precipitate after the first ignition a rapid removal of carbon is effected.

Solutions of hydrofluoric acid to which an excess of boric acid has been added have only a slight solvent action upon glass, even on boiling. Nevertheless, those precipitates which were obtained from such solutions were tested for the presence of silica. A portion of the ignited stannic oxide was transferred to a platinum crucible and brought to constant weight. A few drops of water and dilute nitric acid, and 5 cc. 48 per cent hydrofluoric acid were added. Upon evaporation and ignition no change in weight occurred.

TABLE I—DETERMINATION OF TIN AFTER PRECIPITATION BY MEANS OF CUPFERRON

Expt.	Tin Taken Gram	Tin Found Gram	Error Mg.	Total Volume Cc.
1	0.1083	0.1087	0.4	300
2	0.2068	0.2066	−0.2	170
3	0.1034	0.1032	−0.2	170
4	0.1216	0.1221	0.5	400
5	0.2138	0.2142	0.4	400
6	0.2068	0.2062	−0.6	500
7	0.1034	0.1036	0.2	250

In the first three experiments no hydrofluoric acid was present.

SEPARATION OF TIN FROM ZINC—Zinc and iron, when originally present in a tin alloy, will be found in the filtrate which contains tin in the course of the analysis by the methods mentioned.[5] Cupferron will of course precipitate the iron with the tin. The amounts of iron in tin alloys are generally small. It seems obvious that the iron oxide could be extracted from the ignited precipitate and its amount determined by a suitable method.

Experiments prove that a very satisfactory separation of tin from zinc is effected by precipitation with cupferron.

A solution of pure zinc sulfate was prepared and standardized, the zinc being weighed as pyrophosphate.

Zinc Solution Taken Cc.	Zinc Found Gram
25	0.1484
50	0.2948
25	0.1481
50	0.2958
Average 25	0.1479

Known portions of the zinc and tin solutions were mixed. The tin was precipitated by means of cupferron, and weighed as oxide.

The determination of zinc in the filtrates was a matter of considerable difficulty. The method cannot be recommended when a rapid determination of the zinc is essential. Zinc was weighed as the pyrophosphate, either after repeated precipitations as the double ammonium phosphate, with intervening filtrations to remove organic matter, or after previous precipitation as the sulfide.

TABLE II—SEPARATION OF TIN FROM ZINC BY MEANS OF CUPFERRON

Expt.	Tin Taken Gram	Tin Found Gram	Error Mg.	Zinc Taken Gram	Zinc Found Gram	Error Mg.
1	0.1034	0.1037	0.3	0.1479	0.1491	1.2
2	0.2068	0.2069	0.1	0.1479	0.1489	1.0
3	0.1448	0.1444	−0.4	0.2958	0.2953	−0.5
4	0.1034	0.1040	0.6	0.1479	Not determined	..
5	0.1034	0.1032	−0.2	0.2958	Not determined	..
6	0.2068	0.2073	0.5	0.1479	0.1484	0.5
7	0.1034	0.1037	0.3	0.2958	0.2956	−0.2

In Experiments 2 and 6 no hydrofluoric acid was present. In these cases the filtrate was evaporated with nitric acid in order to destroy organic matter. The nitric acid was then expelled at the temperature of boiling sulfuric acid. The general conditions were similar to those of the experiments recorded in Table I.

SEPARATION OF TIN FROM MANGANESE, ZINC, COBALT, AND NICKEL—It seemed obvious that cupferron would separate tin from any or all of these metals. Solutions were prepared which contained known amounts of tin and from 0.1 to 0.15 gram each of manganese, nickel, cobalt, and zinc. Only the tin was determined.

Tin Taken Gram	Tin Found Gram
0.1034	0.1035
0.2068	0.2073

Greetings Exchanged

While the Leather Division was in session at Milwaukee, delegates from other parts of the world were already proceeding to Barcelona, Spain, to attend the international meeting of the Society of Leather Trades Chemists. In view of the unity of purpose of the two organizations, the Leather Division authorized the sending of the following message by cable:

> SOCIETY OF LEATHER TRADES CHEMISTS, CALLE URGUL 187, BARCELONA, SPAIN: The Leather Division of the American Chemical Society in congress assembled at Milwaukee sends greetings and best wishes for a successful meeting. (*Signed*) JOHN ARTHUR WILSON, Chairman.

Later the following reply was received by cable:

> The Society of Leather Trades Chemists in conference thanks the Leather Division of the American Chemical Society for its greetings and good wishes which are heartily reciprocated.
>
> (*Signed*) E. SCHELL, President.

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[17] THIS JOURNAL, **12,** 344 (1920).

[18] *J. Am. Chem. Soc.*, **41,** 276 (1919). A bibliography of the uses of cupferron is given.

[19] *Compt. rend.*, **170,** 995 (1920).

[20] See references cited by Lundell and Knowles, *loc. cit.*

[21] Fresenius, *Z. anal. Chem.*, **50,** 37 (1911), describes a similar series of transformations of the iron salt of cupferron.

Carbon Dioxide Content of Beverages[1]

A Rapid Method for Determination of Carbon Dioxide in Lightly Carbonated Beverages

By Joseph Cannizzaro

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THE writer has had occasion to estimate the carbon dioxide content of beverages, especially near-beer, and has resorted to gas-volumetric and gravimetric methods such as can be found in standard books of analysis. For the most part these are either long and tedious or require one well versed with the method in order to obtain reliable results.

Of the gravimetric methods, that of Crampton and Trescot[2] was found to be the simplest and comparatively most compact. A modified form of their apparatus was used to check the results of the writer's rapid method. In principle their method consists in connecting the bottle of beverage with a standard carbon dioxide absorption apparatus and absorbing the gas in some weighed U-tubes; the difference in weight representing the carbon dioxide. This method is tedious and requires at least an hour for its proper execution, and even then the results obtained are not very reliable. Hence to an analyst who is called only once in a while to perform such an analysis its application is not very satisfactory. Obviously, the results of the gas-volumetric method are not accurate, owing to the fact that the carbon dioxide, usually collected over water, is absorbed by the latter to a considerable extent and thus vitiates the results.

The rapid method is based on the same principles as Warder's method[3] for the determination of a carbonate in the presence of a bicarbonate. It consists in quickly pipetting a definite volume of the well-cooled beverage and transferring, tip of the pipet under reagent, to a measured volume of standard sodium carbonate. The carbon dioxide reacts:

$$Na_2CO_3 + H_2O + CO_2 = 2NaHCO_3$$

The sodium bicarbonate being neutral to phenolphthalein at a fairly low temperature while the sodium carbonate is alkaline, the unused carbonate may be titrated with standard acid to the disappearance of the pink color, if the titrated solution is kept at about 3° to 4° C.

As carbonated beverages contain more or less fixed acid, a correction must be applied for their presence. This is easily determined on a separate portion of the sample by boiling to expel the carbon dioxide, cooling, and titrating with the sodium carbonate solution, using phenolphthalein as the indicator. The volume of sodium carbonate used is subtracted from the total volume used before in order to obtain the volume really used up by the carbon dioxide.

If the very cold beverage cannot be opened without manifest loss of gas, as indicated by excessive foaming and spilling over, this method cannot very well be applied. In the experience of the author this is of rare occurrence, especially when dealing with near-beer and other cereal beverages.

Specifically, the method found most adaptable for bottled near-beer and similar beverages is as follows:

PROCEDURE

The beer is first thoroughly cooled by means of cracked ice and salt in a pail of suitable size. While cooling, two burets are filled, one with 0.2 *N* sodium carbonate and the other with 0.2 *N* hydrochloric acid, the latter having been standardized against the former. Thirty cubic centimeters of the sodium carbonate are then measured out in a 600-cc. beaker. This and a 25-cc. pipet are placed nearby for rapid availability. When the bottle is cold and is still surrounded by ice, it is carefully and quickly opened, without causing the least agitation to its contents, by means of a common bottle opener. The 25-cc. pipet is then quickly inserted into the bottle and the beverage carefully measured and transferred to the sodium carbonate solution, tip of the pipet below the surface of reagent. The gas is seen to be readily absorbed. The solution is then diluted to about 400 cc. with freshly boiled and cooled distilled water (to about 5° C.). One cubic centimeter of phenolphthalein indicator is then added and slowly titrated with the 0.2 *N* hydrochloric acid to the disappearance of the pink color. Twice the volume of the hydrochloric acid used is subtracted from the 30 cc. of the sodium carbonate in order to obtain the volume of the latter really used up by the carbon dioxide and fixed acids. It is clear from the reaction

$$Na_2CO_3 + HCl = NaHCO_3 + NaCl$$

that the volume of hydrochloric acid used with phenolphthalein as the indicator is one-half the volume of the sodium carbonate present of the same normality.

To determine the fixed acids, another 25-cc. sample is placed in a 600-cc. beaker, diluted to 100 cc. and brought just to a boil, avoiding prolonged boiling. It is then cooled by placing in the cracked ice and salt bath, diluted to 400 cc. with very cold distilled water, and titrated with 0.2 *N* sodium carbonate using phenolphthalein as the indicator to the appearance of a pink color. This volume of sodium carbonate used is then subtracted from the total volume used in the first titration in order to obtain the volume of sodium carbonate used for the carbon dioxide. One cubic centimeter 0.2 *N* sodium carbonate equals 0.0044 gram carbon dioxide.

Although it is highly desirable, when opening the cold bottle containing the sample, to draw the sample in the pipet as rapidly as possible, too much suction must not be applied with the lungs, lest the pressure on the surface of the beer in the pipet be so decreased as to cause evolution of gas. The rate of drawing must be reasonably regulated. This must be kept in mind with beverages containing foaming compounds, as these have a special tendency to foam in the pipet. In such cases, provided the beverage is thoroughly cold, the foam may be disregarded and sucked directly into the mouth. After the proper volume of beverage has been drawn, it may be expectorated.

Apparently, an error is introduced in the process of transferring the sample from the bottle to the standard solution, but it is very low, well within the limits of negligence. Moreover, this minute error is inherent in every method of determining carbon dioxide in beverages, contained in bottles sealed with the so-called crown corks.

Some beverages are highly colored so that a smaller sample or a larger dilution, or both, must be employed in order to observe the end point properly.

After some practice the analyst can judge the amount of sample to use and the dilution necessary to secure a solution suitable for titration.

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[1] Received June 12, 1923.

[2] *U. S. Dept. Agr., Bur. Chem., Bull.* **107**.

[3] *Am. Chem. J.*, **3**, No. 1 (1881).

In ordinary beverages like near-beer the specific gravity may be taken as 1.025, but if the beverage is somewhat thick it is best to determine it and apply correction accordingly. The specific gravity, however, can generally be neglected in the calculation, as the error incurred is quite inappreciable.

RESULTS AND COMPARISON WITH GRAVIMETRIC METHOD

The results of this method have been repeatedly checked against those obtained by the Crampton and Trescot method, and the checks are reasonably within the limits of experimental error.

The following table shows eight analyses with a comparison of the gravimetric and the rapid methods:

	PER CENT—CARBON DIOXIDE		
Sample	Gravimetric Method	Rapid Method	Difference
1	0.386	0.385	0.001
2	0.410	0.402	0.008
3	0.399	0.395	0.004
4	0.300	0.306	0.006
5	0.420	0.412	0.008
6	0.450	0.444	0.006
7	0.376	0.366	0.010
8	0.350	0.358	0.008

The first six samples were near-beer and the last two popular brands of soda water.

The same method, with slight modifications, is found in the Official Methods of the Association of Official Agricultural Chemists[4] for determining carbon dioxide in mineral waters.

[4] Assoc. Official Agr. Chem., Methods, **1920**, p. 28.

Applications of Vapor Pressure Measurements[1]

By H. S. Davis and Mary D. Davis

ARTHUR D. LITTLE, INC., CAMBRIDGE, MASS.

A convenient vapor pressure apparatus consists of two similar glass flasks connected to a manometer tube and means whereby sealed glass containers full of liquids may be broken inside the flasks. Full details for the manipulation of such a device are given.

In the recovery of light oils from coke-oven gas by oil scrubbing, the light oil vapors are to a certain extent absorbed as a whole, and selective absorption plays a smaller part than might be expected. This fact may be partly due to differences in the rates of diffusion of the vapors, the lighter ones tending to outstrip the heavier in their race to the absorbent oil.

It is possible to check up the efficiency of a light-oil recovery plant by measuring the total partial pressure of the light oils in the gas at various points in the system, and also their tension from the absorbent oil.

IN PREVIOUS publications[2] the writers have described a differential vapor pressure apparatus. Further experimentation and the introduction of the device into commercial work have led to improvements in its design along the lines of durability and ease of manipulation.

APPARATUS

The apparatus (Fig. 1) consists of two similar glass flasks, each with a ground-glass stopper and a capillary side tube, with stopcocks, connected to a manometer tube. Each flask is provided with a metal device whereby a small, sealed, glass container may be broken inside it. The following improvements are included in the design shown in the figure:

MANOMETER TUBE—This was formerly connected to the flask to form one rigid piece. The writers have found, however, that joints of rubber tubing at the points shown in the figure do much to relieve strain on the apparatus, and also permit manometer tubes of different lengths to be used on the same apparatus.

CONTAINERS FOR LIQUIDS—Formerly the liquid whose vapor pressure was being measured was put into small glass bulbs which were attached to movable rods so that when desired the bulb could be broken against the bottom of the flask. The containers now used are made from pieces of thin-walled tubing of 1 to 1.5 cm. outside diameter. The tubing is drawn to a capillary at one end and sealed off 1.5 cm. from the bulb. At the other end it is drawn to a somewhat larger capillary, which is cut off about 2 cm. from the bulb and left open for filling.

The metal breaking device has a holder to support the container in a vertical position inside the flask. When it is desired to release the liquid into the flask, the lower part of the breaking device is grasped with the left hand while the upper part is twisted with the right. This movement, acting on a simple contrivance, breaks off both the slender ends from the glass container and allows the liquid to flow evenly into the flask. If any trouble is encountered in breaking off the capillary ends, it may be entirely eliminated by scratching them, before filling, with a file at the desired points.

FILLING THE CONTAINERS—In previous descriptions detailed instructions have been given for filling small containers by alternate heating and cooling or by alternate lowering and raising of the air pressure. However, these methods are open to the following objections:

1—In the case of high-boiling liquids it is necessary to heat them so hot, in order to obtain a vapor pressure sufficient to drive the air from the bulb, that decomposition may begin. On the other hand, their vapor tensions at ordinary temperatures are so low that filling the bulb by changes of pressure is a slow process.

2—In dealing with a liquid mixture there is a tendency to fractional distillation of the liquid in the bulb.

3—Occasionally a bulb bursts through a too rapid change of pressure. Sometimes the loss of material in this way is a serious matter.

During recent investigations such methods of filling have been completely discarded and instead a capillary pipet, made by pulling out a piece of narrow tubing at one end, has been used. An outside diameter of 0.5 mm. for the capillary will enable ordinary liquids to be drawn with ease through a piece several centimeters long, and the inside diameter of the stem of the container through which it must pass need be very little larger. Such pipets made from glass tubing of 3-mm. inside diameter, and provided with a graduation mark, have been a great convenience for introducing accurate amounts of liquids into small containers of various kinds.[3]

SEALING THE CONTAINERS—To seal successfully the open stem of the container, filled with a volatile liquid, it is first heated evenly in a small flame, about 1 cm. from the bulb, and drawn out to a minute capillary. The container is now put aside and allowed to cool completely, after which the capillary

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[1] Received February 12, 1923.

[2] THIS JOURNAL, **10**, 707 (1918); Advisory Council for Scientific and Industrial Research of Canada, Report 2 (1918).

[3] A capillary pipet of this kind should be of great use in many physicochemical operations where it is necessary to introduce measured quantities of liquids into small glass containers which are to be sealed up afterwards in the blowpipe. For instance, measurements of vapor density in the Victor Meyer apparatus, of compressibility by certain methods, and of heats of combustion in the Bertholet bomb are made on liquids preferably after enclosing them in such containers.

end may be sealed off without disturbing the air pressure inside. Except in the case of very volatile liquids, it is not necessary or even desirable to seal off this final capillary at all, in which case the breaking device may be arranged to break off only the lower stem of the container.

Quantity of Liquid in Container—When dealing with a homogeneous liquid such as pure benzene, the actual vapor pressure developed in the apparatus is independent of the quantity of liquid used; but in the case of a mixture of two or more liquids, the vapor pressure developed is seriously affected by this factor. This is due to the fact that the partial evaporation into the flask, which takes place after the bulb is broken, somewhat changes the composition of the residual liquid. The part which evaporates is richer in volatile constituents than the remainder, so that the final vapor tension of the residual liquid is somewhat lower than the true vapor tension of the original liquid in the bulb. This error is present in all measurements of vapor pressure by the static method. When the composition of the vapor is known, the necessary correction can easily be calculated.

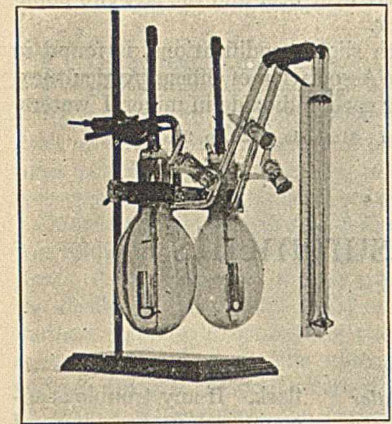
Fig. 1

It will be found convenient, for all measurements of the vapor tension of liquids in this apparatus, to have the volume of liquid used one one-hundredth that of the volume of the flask.

Putting in the Stoppers—The sealed containers are placed in the supports on the lower ends of the rods through the stoppers. The stoppers are slightly greased, put in place, and secured by small, stout rubber bands over the lugs. It is not necessary to wire in the stoppers.

Water Bath—The flasks of the apparatus are immersed in a liquid bath until half their necks are covered, while the manometer tube remains outside.

Cleaning the Apparatus—After the determination is completed the stopcock in the manometer is closed, the other stopcocks are opened, and the stoppers removed. The flasks are cleaned by wiping all grease from the insides of the necks and sucking out any remaining liquid through a small glass tube connected with the suction pump. They are then rinsed with a little benzene or alcohol, which is afterwards sucked out. Between the apparatus and the suction pump there should be a small safety bottle to catch fragments of glass. Each of the flasks is then throughly cleaned of vapor by drawing air through it for at least 15 minutes in the following manner: A cork stopper, through which has been fitted a glass tube reaching nearly to the bottom, is placed in the flask. Suction is now applied to the stopcock and air is drawn in through the glass tube to the bottom of the flask and out at the stopcock.

Caution—It is of the utmost importance that the apparatus be kept clean from any liquid of the kind whose vapor pressure is being determined. The stoppers must be removed from the apparatus as soon as the experiment is completed. If they are left for long periods in the flask containing a volatile liquid, its vapor may penetrate the connecting tubes and rubber connections, causing trouble.

Specific Directions for Measuring the Vapor Tension of a Liquid

(*a*) Fill a container with a measured quantity of liquid.
(*b*) Place it in the support attached to the right-hand stopper and insert the stoppers in the flasks.
(*c*) Put the apparatus in the water bath. Open both stopcocks to the air in order to bring the pressures in both flasks to atmospheric, then open the manometer stopcock and close the other two.
(*d*) Read the manometer levels, estimating with the eye to tenths of millimeters, at 5-minute intervals until the readings are constant.
(*e*) Break the container.
(*f*) Read the manometer levels at intervals until they are constant.
(*g*) Close the manometer stopcock, open the other stopcocks, remove the stoppers, and clean the apparatus.
(*h*) Read the temperature of the bath and the barometer pressure.

The difference between the final and initial readings gives the vapor tension from the liquid in terms of the manometer liquid. If the absolute value of this pressure is desired, certain obvious corrections must be applied. The largest of these arises from changes of air pressure in the two flasks caused by the movement of the manometer liquid. This correction is of special importance when a light liquid is employed and, in some cases, may amount to 25 per cent of the total reading.

The following measurements carried out on the tension of light oil from a sample of stripped oil from a well-operated American plant will illustrate the method:

Time Min.	Pressure in Millimeters of Oil (Sp. Gr., 0.86) No. 1	 No. 2
0 (Put apparatus in bath)	3.1	1.5
5	1.7	1.2
10	0.7	0.6
16	0.4	0.4
20	0.2	0.1
25	0.1	0.0
30 (Apparatus at equilibrium and ready for experiment)	0.0	0.0
0 (Broke bulb of oil in flask)	0.0	0.0
5	3.6	3.3
10	3.7	3.9
15	3.8	4.1
25	3.9	4.2
Pressure developed	3.9	4.2
Correction fpr changes in air pressures in flasks	0.9	0.9
Total pressure	4.8	5.1
Pressure in millimeters of mercury	0.30	0.32

Diffusion of Vapors and Its Relation to Absorption Processes

The rates at which vapors are disseminated by true diffusion and by convection currents are very different, as the following striking experiment will illustrate:

Fix firmly in one of the supports a container completely open and unrestricted at the top. Fill this with a volatile liquid to within a few millimeters of the brim and leave it unsealed. Then lower the stopper gently into place in the flask. It will be found that the development of pressure is surprisingly slow. Now break the lower stem of the container, thus allowing the liquid to flow over the bottom of the flask. The usual rapid development of pressure, caused mainly by convection currents, will result.

It is well known that the evaporation of a liquid into a gas at rest is determined principally by the rate of diffusion of its vapor through the gas which lies above it, and similar considerations must apply to the absorption of its vapor into a nonvolatile medium. It would reasonably follow that the rates at which two vapors are simultaneously absorbed from a gas into another medium must be somewhat influenced by the difference in their rates of diffusion in the gas. This difference is greater than that between their rates of diffusion separately in the gas, according to the curious law, first pointed out by Graham, that the movement of the faster is accelerated and that of the slower retarded in simultaneous diffusion.

Of course, if equilibrium were reached at each point in the absorption system, Raoult's law and the law of partial pressures would hold. On the other hand, if equilibrium is not attained, there should be a tendency for the heavier and less diffusible vapor to be retained in the gas. It will be readily seen that such an effect would oppose selective absorption.

TESTING EFFICIENCY OF BENZENE (LIGHT OIL) SCRUBBERS[3]

If selective absorption of the various light oil vapors took place to any great extent in an ordinary scrubber, then the relative proportions of the constituents of the light oil in the absorbent oil would vary at different points, the higher boiling constituents predominating in the first part of the washing system.[4]

The selective absorption effect is much less than might be expected, and perhaps this can be explained by the diffusion effect pointed out above. But whatever the explanation, the fact remains that in an ordinary light oil scrubber the benzene and toluene, to a certain extent, are absorbed, not in inverse proportion to their volatility, but as a whole. It requires prolonged contact between the absorbing medium and the gas to effect a separation of the two vapors.[5]

For this reason vapor pressure measurements can be successfully applied to the control of light oil scrubbers in the following ways:

1—The relative efficiencies of the different units can be compared by measuring the tension of light oil from samples of wash oil taken from various points in the system.

2—The measurements in No. 1 can be checked by measuring the pressure of the residual light oil in the gas at these same points.

3—The efficiency of the stripping still can be checked by measurements of the tension of light oil from the debenzeneized oil. This is an important measurement because no amount of scrubbing will ever reduce the benzene content in the gas below a pressure equal to the tension of light oil from the debenzeneized oil.

The measurement of the vapor tension of light oil from an absorbent oil is a comparatively easy matter and has already been described.

Comparative measurements of the total pressure of light oil in the gas at various points in the system are carried out in the following manner: Into each flask of the vapor pressure apparatus is put a sealed container filled with an accurately measured quantity of liquid benzene. (It is recommended that the volume of benzene used be one one-hundredth of the volume of each flask.) One flask of the apparatus is then filled with the gas to be analyzed and the other is left full of air. When the two containers are broken simultaneously, the differential pressure which develops between the two flasks is proportional to the vapor pressure of light oil originally present in the gas. The theory of these measurements has already been dealt with in previous publications.[2] The writers failed, however, to lay enough stress on the importance of measuring *equal* volumes of benzene into the containers in each experiment and of preserving the same ratio between the volumes of benzene and of the flasks in separate experiments.

In 1917 tests were carried out with this apparatus on a light oil recovery plant operating under war conditions on coke-oven gas in Canada. The absorption system comprised six large washing towers of the hurdle type in series, through which the gas and wash oil were passed in countercurrent contact. In 1918 further tests were carried out. During the intervening period centrifugal sprays had been introduced before each of the first three towers in a vain attempt to increase the recovery.

The experienced operator of a modern benzene-recovery plant will at once perceive that this was a very inefficient recovery unit, and indeed, in view of the results obtained from these tests, radical changes were planned in it which were only cut short by the armistice.

A summary of the results from these tests is given in Table I.

DISCUSSION OF RESULTS

Through the greater part of the absorbing system, the vapor tension of light oil from the wash oil was nearly equal to the partial pressure of light oil in the gas at the corresponding point. Indeed, the wash oil in the third tower actually gave up benzene to the gas, a condition which was traced to its relatively higher temperature there.

In spite of the superabundance of washing, a large part of the benzene passed through the towers unabsorbed. This condition was caused by the inefficiency of the stripping (Hirzel) still, which left a large percentage of light oil in the poor or debenzeneized oil. No amount of washing will ever compensate for inefficiency in the still.

The quality of coke-oven gas delivered to this plant varied much in quality. On May 13 the superintendent was annoyed by the small output of light oil, whereas on the 17th the yield was excellent. As will be evident from the table, these discrepancies were caused, not by any change in the efficiency of the benzene-recovery unit, but by variations in the quality of the gas.

GASOLINE AND SOLVENT RECOVERY

Many of the principles of benzene recovery are embodied in processes for the recovery of gasoline from natural gas or still vapors. There is, however, this difference, that the benzene is rather sharply defined from the other constituents of coke-oven gas in chemical and physical properties, whereas the dividing lines between the constituents of natural gas are much less clearly marked, and the properties of the gasoline are greatly influenced by the methods of recovery. However, a study of the vapor pressures involved cannot fail to throw light on any system for gasoline or solvent recovery.

TABLE I—VAPOR PRESSURE MEASUREMENTS ON THE SCRUBBING TOWERS (SIX TOWERS AND THREE SPRAYS, IN SERIES) OF A LIGHT OIL-RECOVERY PLANT

SAMPLE	LAST POINT IN SCRUBBERS PASSED BY GAS	September, 1917	May 6, 1918	May 13, 1918	May 14, 1918	May 17, 1918	May 18, 1918
Rich oil	......	...	6.1	...	...	...	...
Rich gas	Entrance	8.4	...	6.1	7.3 7.7 } 7.5	10.3 (5.3)	5.4
Gas from Tower 1	1st spray	...	7.5 6.0 } 6.8	...	7.0	(4.3)	(4.2)
Gas from Tower 2	Tower 1 (2nd spray)	6.2	5.7	...	5.2	...	...
Gas from Tower 3	Tower 2 (3rd spray)	4.6	3.1 3.0 } 3.1	...	5.0	...	...
Gas from Tower 4	Tower 3	5.0	3.5 3.5 } 3.5	...	5.0	...	...
Gas from Tower 5	Tower 4	4.8	3.6 3.5 } 3.5	...	4.8	...	...
Gas from Tower 6	Tower 5	3.7	3.0 3.6 } 3.3	...	...	...	...
Poor gas	Tower 6	3.3	2.5 2.7 } 2.6	4.3	4.2	5.8 (3.9)	(2.2) (2.4) } 2.3
Poor oil	From Hirzel still	...	3.0	...	...	...	...

In the case of a gas, the figures represent the total partial pressures of the light oil vapors in millimeter of mercury; in the case of an oil they refer to vapor tensions of light oil in millimeter of mercury. The figures in parenthesis indicate partial pressures of pure benzene (C_6H_6).

The table shows:

1—That the light oil content of the coke-oven gas varied from day to day.

2—That no absorption was taking place in Towers 3, 4, and 5.

3—That about one-third of the light oil passed through the scrubbing system unabsorbed.

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[4] Cantello, *Can. Chem. Met.*, **6**, 196 (1922).

[5] Sperr, *Gas Age*, **41**, 393 (1918).

Preliminary Examination of Water Samples[1,2]

Calcium and Sulfate by Turbidity and Hardness by the Soap Method

By W. D. Collins and Margaret D. Foster

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The preliminary examination of a water sample will save time in making a complete mineral analysis, and may show that a complete analysis is not necessary. The examination will include titrations of chloride and alkalinity by the usual methods, turbidimetric determinations of sulfate and calcium by comparison with standards in test tubes, and sometimes a determination of hardness by the soap method.

The turbidimetric tests are made with volumes of 10 cc. for the sample and standards. For the sulfate precipitation 1 cc. of acid barium chloride solution is used (48 cc. of hydrochloric acid, specific gravity 1.19, and 100 grams of $BaCl_2.2H_2O$ in 1 liter). For calcium 1 cc. of acetic acid (equal parts of 99.5 per cent acid and water) is added, the solution is shaken, 1 cc. of potassium oxalate solution (0.2 gram $K_2C_2O_4$ per cc.) is added, the solution is shaken again and after 10 minutes the turbidities are compared.

Tests of one hundred seventy-four waters varying in composition over a wide range show that the preliminary results for sulfate, calcium, and hardness are reasonably close to the results obtained in the complete analysis. In general, the error is likely to be about 10 per cent of the quantity determined, and may be plus or minus. For preliminary examinations or for field work[3] this accuracy is sufficient.

In a laboratory where samples of water received for analysis may contain from 25 to 25,000 parts per million of dissolved mineral matter, it is well worth while to make a preliminary examination before proceeding to evaporate the part of the sample that is to be used for the complete mineral analysis. The preliminary examination ordinarily involves the determination of the acid radicals present in considerable quantities and the calcium and magnesium or their equivalent. From these results it is possible to calculate the sodium needed to balance the analysis and thus have roughly a complete analysis.

In most natural waters the only acid radicals to be considered are chloride, sulfate, and bicarbonate or carbonate. Only a few waters contain enough nitrate to enter into the calculation of the quantity of sodium, or to cause the solution of platinum when the waters are evaporated with hydrochloric acid in a platinum dish. It is always well, however, to determine the nitrate before the acidified sample is evaporated. The regular methods for the titration of chloride and bicarbonate are sufficiently rapid to serve for the preliminary examination. Sulfate is the only acid radical for which a special method must be used in the preliminary examination.

The determination of total hardness of a water by the soap method gives a measure of the combined calcium and magnesium and serves as a basis for calculation of the sodium. A turbidimetric determination of calcium takes less time than a soap test and often is sufficient for determining the quantity of a sample to take for evaporation.

In order to have definite data in regard to the reliability of simple turbidimetric sulfate and calcium determinations and the soap test as applied in regular laboratory work, these three tests were made on each of a series of one hundred seventy-four samples which were analyzed in the Water Resources Laboratory of the U. S. Geological Survey over a period of about a year. The results of these tests as discussed below, and as shown in Figs. 1, 2, and 3, demonstrate the usefulness of the methods for preliminary examinations. The data show clearly that the methods as used cannot be trusted to give results that can be used in place of regular analytical determinations. If greater accuracy is desired without making a complete analysis, it can be obtained by using the rapid methods described by Hale,[4] or by using the turbidimeter in the determination of sulfate and calcium. The turbidimetric determinations described below are made without the turbidimeter and require only 10 cc. or less of the sample.

Sulfate

Estimation of quantities of sulfate by the turbidity produced on the addition of barium chloride to an acidified solution is probably one of the oldest of the simple rapid quantitative methods. A number of authors[5] have described various ways of increasing the accuracy of the turbidimetric determination of sulfate, and it is probable that in many laboratories where large numbers of routine sulfate determinations are made the results obtained with the turbidimeter are as accurate as gravimetric results. Such accuracy is not generally found in the results of turbidimetric determinations of sulfate in miscellaneous samples of water, nor is it necessary in preliminary examinations. Equally useful results are obtained by the simple procedure outlined below.

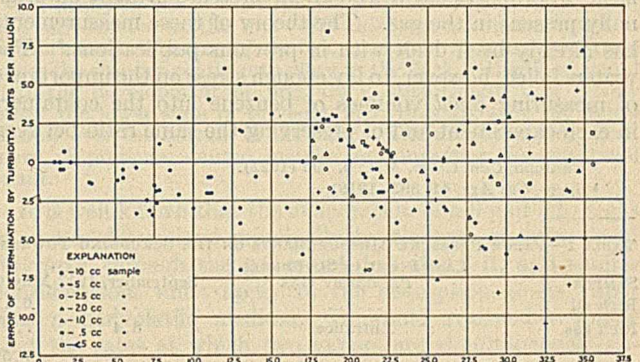

Fig. 1—Errors in Determinations of Sulfate by Turbidity

Samples of 10 cc. are taken in test tubes (100 × 10 mm.) and standards are made up containing from 0.05 to 0.35 mg. of sulfate (SO_4) in 10 cc. To each tube is added 1 cc. of an acid solution of barium chloride (48 cc. of hydrochloric acid of specific gravity 1.19 and 100 grams of $BaCl_2.2H_2O$ in 1

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[1] Received May 4, 1923.

[2] Published by permission of the Director, U. S. Geological Survey.

[3] Collins, "Field Examination of Water," special circular, U. S. Geol. Survey, March, 1922.

[4] *J. Am. Chem. Soc.*, **29**, 1078 (1907).

[5] Hinds, *Ibid.*, **18**, 661 (1896); **22**, 269 (1900); Jackson, *Ibid.*, **23**, 799 (1901); Muer, This Journal, **3**, 553 (1911).

liter). The tubes are shaken vigorously and the turbidities compared by looking through the depth of the liquid at a black background. If the sample contains over 35 parts per million of sulfate, a smaller portion is diluted to 10 cc. with distilled water. If the sulfate is over 700 parts per million, a dilution is made and the proper quantity of the diluted sample is taken for the determination.

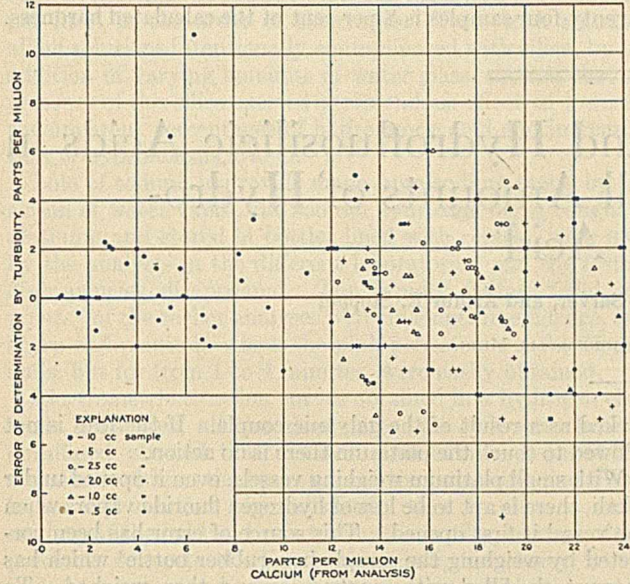

Fig. 2—Errors in Determinations of Calcium by Turbidity

Fig. 1 shows the differences between the sulfate found by the rough turbidimetric method and the quantity found by the regular gravimetric method in the course of the complete analysis. The complete analyses all balanced well enough to indicate that the differences were due almost entirely to the error of the turbidimetric comparisons. The points which represent 10-cc. samples show the actual quantity of sulfate determined by analysis plotted against the difference between this quantity and that determined by turbidity. For the points representing samples of 5 cc. the analytical result has been divided by 2 and plotted against half the difference between the gravimetric and turbidimetric results. Similar reduction has been made for the smaller samples.

The average of the percentage differences for all the samples is 16 per cent of the analytical results. For the seventy-seven samples of 10 cc. the average difference of 22 per cent corresponds to only 2.4 parts per million of sulfate (SO_4), which is of no practical significance. An average difference of 12 per cent for the fourteen samples of 0.5 cc. represents an average difference of 50 parts per million of sulfate, which is considerably more than the allowable error in the gravimetric determination of from 350 to 700 parts per million of sulfate. The turbidimetric determination of sulfate in test tubes is thus shown to be sufficiently accurate for a preliminary examination of a water sample, but not reliable enough to take the place of a gravimetric determination. It calls for no special apparatus, is rapid, and requires only a small sample, which is sometimes an important consideration.

CALCIUM

Although the turbidimetric determination of calcium after precipitation with ammonium oxalate in neutral solution was reported by Hinds[5] to give accurate results, the method has not been found generally applicable to natural waters. A number of experiments were made with oxalic acid and potassium oxalate to find the proportions which would give the most accurate turbidimetric determination of calcium, but the best proportions of these reagents did not give results of the accuracy of the turbidimetric determination of sulfate. When acetic acid was substituted for oxalic acid much better results were obtained. The results of a large number of tests with different quantities of the reagents led to the selection of the details of the method given below.

Samples of 10 cc. of the water to be tested are taken in test tubes and standards are prepared in other tubes containing in 10 cc. from 0.04 to 0.24 milligram of calcium. To each tube 1 cc. of acetic acid (equal volumes of 99.5 per cent acid and water) is added and the contents are well shaken. After the addition of 1 cc. of potassium oxalate solution (containing 0.2 gram $K_2C_2O_4$) the tubes are again shaken. The turbidities are compared after 10 minutes. The relative turbidities are quite constant for 3 or 4 hours, so it is not necessary to make the comparison at once. The upper limit for the determination of calcium as described is about 24 parts per million. Samples of less than 10 cc. are taken for the more concentrated waters, as is done for sulfate, and the volumes made to 10 cc. before the addition of reagents.

The differences between the analytical results and the turbidimetric results for calcium in one hundred seventy-four samples of water are shown in Fig. 2. The differences and the analytical results are divided by the appropriate factors for the samples of which less than 10 cc. were used for the turbidimetric determination. It is evident that the accuracy is about the same as for the determination of sulfate. The average percentage error is 19 per cent of the analytical result. The error of 28 per cent for the sixty-eight samples of 10 cc. corresponds to an average error of 2.2 parts per million of calcium, which is not generally of any significance.

The results shown in Fig. 2 make it plain that the turbidimetric method described is sufficiently accurate for a preliminary determination, but cannot be depended upon to give results that can be used with the same confidence as the results obtained by the ordinary analytical methods.

HARDNESS

The soap method for hardness, practically as originally devised by Clark,[6] is recognized in all texts as useful for approximate determinations. Some of the criticisms of the method have been based on results obtained with details of manipulation different from those generally recommended, and therefore do not apply to the method as now used.

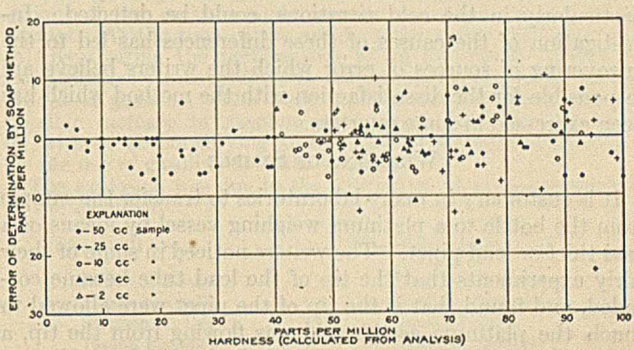

Fig. 3—Errors in Determinations of Hardness by Soap Method

In the preliminary examination of the one hundred seventy-four samples for which sulfate and calcium were determined by turbidity, the hardness was determined by following every

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[6] "Repertory of Patent Inventions for 1841," London, 1849; *Chem. Gaz.*, **5**, 100 (1847).

detail of the soap method as given in Standard Methods of Water Analysis of the American Public Health Association. If the hardness of a sample was over 100 parts per million, less than 50 cc. were taken for the test and the volume made up to 50 cc. with distilled water.

The hardness of each water was calculated from the calcium and magnesium determined in the regular analysis. The difference between the determined and calculated hardness for each sample is plotted against the calculated hardness in Fig. 3. The errors for determinations above 100 parts per million have been divided by a factor corresponding to the quantity of water used in the soap test, as was done with the sulfate and calcium results.

It is evident that the soap method for hardness is more reliable than the rough turbidimetric methods for sulfate and for calcium. The average percentage or difference between the calculated and determined hardness for the one hundred seventy-four samples is 8 per cent of the calculated hardness.

The Titration of Hydrofluoric and Hydrofluosilicic Acids in Mixtures Containing Small Amounts of Hydrofluosilicic Acid[1]

By Paul H. M.-P. Brinton, Landon A. Sarver, and Arthur E. Stoppel

University of Minnesota, Minneapolis, Minn.

THE determination of hydrofluoric and hydrofluosilicic acids in mixtures of the two has been investigated by a number of workers,[2] and the problem is of considerable importance because it is really encountered in every analysis of the hydrofluoric acid of commerce. A study of the method given by Scott[3] forms the subject of this paper.

In this method the sample of the mixed acids, to which has been added some potassium nitrate, is first titrated ice cold with standard sodium hydroxide, using phenolphthalein as indicator; and then the titrated solution is heated to about 80° C., and again titrated to a pink end point. The reactions for these two titrations are as follows:

For the cold end point:

$$H_2F_2 + 2NaOH \longrightarrow 2NaF + 2H_2O$$
$$H_2SiF_6 + 2KNO_3 + 2NaOH \longrightarrow K_2SiF_6 + 2NaNO_3 + 2H_2O$$

For the hot end point:

$$K_2SiF_6 + 4NaOH \longrightarrow 4NaF + 2KF + Si(OH)_4$$

From the equations the results of the titrations for the two acids are readily calculated.

Results of analyses of the same sample made in three different laboratories by this method showed wide divergence. Not only were the final results at variance, but there was considerable difference in the ease with which the end points, particularly in the cold titrations, could be detected. Investigation of the causes of these differences has led to the uncovering of sources of error which the writers believe are responsible for the dissatisfaction with the method which has been expressed in some quarters.

Weighing of Sample

It is customary in many laboratories to transfer the sample from the bottle to a platinum weighing vessel by means of a lead thief or lead pipet. The writers noticed in some of their early experiments that the tip of the lead tube became corroded, and found that if the tip of the pipet were allowed to touch the platinum as the acid was flowing from the tip, a brisk evolution of gas occurred and the lead was rapidly attacked as a result of the galvanic couple. If the lead is not allowed to touch the platinum there is no action.

With small platinum weighing vessels, even if opened under alkali, there is apt to be loss of hydrogen fluoride vapors when the vessel is first opened. This source of error has been corrected by weighing the sample in a rubber bottle[4] which has been nearly filled with cracked ice and then weighed. To overcome the change of weight due to condensation of moisture on the cold bottle during weighing, the bottle is weighed in a stoppered weighing bottle, well lined with asbestos paper, and counterpoised by a weighing bottle of similar external form on the opposite balance pan. After weighing, the bottle is shaken once or twice to absorb any vapors of hydrogen fluoride, and the sample, then in the form of an ice-cold, dilute solution, can be poured and rinsed into the alkali without loss.

End Point and Indicator

Methyl orange cannot be used because of the weak nature of the second hydrogen of H_2F_2. This leads to the formation of acid salts as intermediate reaction products, which have the strength of weak organic acids. Phenolphthalein, however, is satisfactory. Scott[3] suggests as the end point for the cold titration a pink that will persist for 15 seconds. It is self-evident that an alkali solution free from carbonate must be used, for even at this temperature the end point with phenolphthalein when using a solution contaminated with carbonate is not only misplaced, but is also faint and fleeting. If the solution is not icecold for the first end point, the color will rapidly fade due to hydrolysis of potassium fluosilicate. Katz[5] has suggested that this hydrolysis proceeds much more rapidly in the presence of calcium salts, owing to disturbance of equilibrium due to formation of insoluble calcium fluoride, and it was thought that perhaps calcium oxide would be inadmissible as a reagent for removing carbonate from the standard alkali; but the amount of calcium oxide which can exist in a sodium hydroxide solution is found to have a negligible effect.

Effect of Silica in the Standard Alkali

Apparently, the most serious source of error in the use of this method is the silica content of ordinary alkali solutions. In tracing out the cause of the divergence in the analytical results obtained in three laboratories on the same sample,

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[1] Presented before the Division of Inorganic and Physical Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] Guyot, *Compt. rend.*, **71**, 224 (1870); Katz, *Chem. Ztg.*, **28**, 356, 387 (1904); Greef, *Ber.*, **46**, 251 (1913); Dinwiddie, *Am. J. Sci.*, **192**, 421 (1916); Huddleston and Bassett, *J. Chem. Soc.* (*London*), **119**, 403T (1921).

[3] "Standard Methods of Chemical Analysis," **1922**, p. 1019, D. Van Nostrand Co.

[4] Hard rubber bottles of 0.5-ounce capacity have been found very satisfactory for this purpose.

[5] *Chem. Ztg.*, **28**, 356 (1904).

it was found that one alkali solution was freshly made, one was several months old, and one was two years old. The carbonate had been recently removed from all the solutions by calcium oxide. The percentages of hydrofluosilicic acid reported by the three laboratories were 1.54, 2.24, and 5.52, in the order of the ages of the sodium hydroxide solutions. A determination of the silica in these standard alkali solutions showed that they contained 0.02, 0.07, and 0.32 gram of silica per liter, in the order of their ages. Tests with standard alkali solutions intentionally contaminated with silica, by the addition of varying amounts of water glass, showed that the presence of this silica exerted a tremendous effect in lowering the apparent percentages of hydrofluoric acid and increasing that of hydrofluosilicic acid.

Lots of sodium hydroxide made from sodium metal by the action of water vapor, the sodium hydroxide being caught in platinum and stored in bottles lined with ceresin, were used by the analysts in the different laboratories, and the former discrepancies disappeared. The rapidly fading "cold end points" of the earlier analyses were no longer in evidence, and sharp end points in which the pink persisted, not for 15 seconds, but for from 1 to 4 minutes, were easily obtained.

Electrometric titration curves obtained in a hydrogen electrode apparatus, all the glass parts of which were heavily paraffined, showed that in the absence of silica in the standard alkali solution the hydrolysis of the potassium fluosilicate in ice-cold solution was sufficiently slow to allow a ready reading of the cold end point, whereas in the presence of appreciable amounts of silica in the alkali, the change in the hydrogen-ion concentration on standing was much more rapid, and the end-point color correspondingly fleeting.

In order to determine quantitatively the exact effect of silica on the analyses, a series of standard alkali solutions of varying silica content were made from sodium metal, with subsequent additions of pure sodium silicate which had been obtained by acidifying sodium silicate solution with hydrochloric acid, boiling off carbon dioxide, mixing with pure sodium hydroxide solution, warming, and filtering. The silica content of these standard alkali solutions was accurately determined gravimetrically.

TABLE I—RELATION OF ANALYTICAL RESULTS TO AMOUNTS OF SILICA IN STANDARD ALKALI SOLUTIONS

Grams SiO_2 per Liter NaOH	Per cent HF Found	Per cent H_2SiF_6 Found
0.036	51.01	2.36
0.180	49.78	4.05
0.252	48.84	4.90
0.396	47.10	6.58
0.536	45.89	8.12

The importance of the effect of silica will be understood when it is realized how rapidly silica is taken up from a glass bottle by a sodium hydroxide solution. As an example, a standard alkali solution freshly prepared showed 0.020 gram of silica per liter. After standing less than four months this solution showed 0.092 gram of silica per liter, which would make a percentage error of nearly 40 per cent in the amount of hydrofluosilicic acid reported in that particular sample.

It will be seen from Table II that the silica in the standard alkali added to the solution up to the cold end point is all converted to hydrofluosilicic acid, and is so registered in the analysis—that is, the silicon tetrafluoride first formed by the action of the hydrofluoric acid on the silica is completely hydrolyzed to fluosilicic acid. Naturally, any silica in the alkali added after the cold end point has been passed would not count, because there would be no free hydrofluoric acid left to react with it. In Table II all samples are calculated to a 1-gram basis for ease of comparison.

The column $c-b$ in Table II, when multiplied by 100, gives the percentages of hydrofluosilicic found in the analyses after deducting the amount of hydrofluosilicic acid equivalent to the silica added in the form of impurity in the standard alkali. These percentages run from 1.92 to 2.04, which for this determination may be considered a satisfactory degree of concordance. The gradual increase in the percentage of (corrected) hydrofluosilicic acid found with increasing amounts of silica introduced as impurity cannot be definitely explained at this time, but it is doubtless connected with the increasing difficulty of detecting the cold end point as the amount of silica increases. It should be noted, however, that with the lower amounts of silica, such as would be found in solutions of reasonable freshness, the deviation is very slight, and it is well within the limit of accuracy of the method.

TABLE II

(a) SiO_2 Added G.	(b) H_2SiF_6 Equivalent to SiO_2 Added G.	(c) H_2SiF_6 Found G.	($c-b$) Corrected H_2SiF_6 G.
0.00182	0.00436	0.0236	0.0192
0.00883	0.02113	0.0405	0.0194
0.01227	0.02936	0.0490	0.0196
0.01898	0.04543	0.0658	0.0204
0.02542	0.06082	0.0812	0.0204

CONCLUSION

In conclusion, if accurate results are desired by this method, it is suggested that a determination of silica be made in even freshly prepared solutions of standard alkali, and that corrections be applied to the figures found for the two acids. One molecule of silica will react with six molecules of hydrofluoric acid to form one molecule of hydrofluosilicic acid. Therefore, the weight of silica added during the titration up to the cold end point should be multiplied by the factor H_2SiF_6/SiO_2, or 2.393, to find the weight of hydrofluosilicic acid to be deducted from the weight of hydrofluosilicic acid found; and by the factor $6HF/SiO_2$, or 1.991, to find the weight of hydrofluoric acid to be added to the weight of hydrofluoric acid found.

Explosion at Bureau of Standards

On the afternoon of September 20, a violent explosion followed by fire occurred in the dynamometer laboratory of the Bureau of Standards. One man was killed instantly, three others were injured so seriously that they died during the night, and four others seriously burned or cut. The heroism of the survivors of the staff in rescuing the injured from the furiously burning wreckage and in shutting off the electric circuits and the ammonia valves, minimized the loss of life and property.

The explosion occurred in the altitude chamber which is used in testing the performance of aircraft engines under the conditions of low pressure and temperature obtaining at high altitudes. At the time of the accident the room was being used in investigating the performance of an automobile engine, at temperatures corresponding to winter operation, using various grades of gasoline. The work was intended to determine the possible increase in gasoline production per barrel of crude oil, with the accompanying conservation of our natural resources, by the use of gasoline of lower volatility.

The explosion was due to the ignition of an explosive mixture in the chamber.

The dead are:

Logan L. Lauer
Urban J. Cook
Stephen N. Lee
Joseph Kendig

The injured are:

Henry K. Cummings
Frank E. Richardson
Roger Birdsell
George W. Elliott
C. N. Smith
R. F. Kohr

Most of these men were college graduates with experience and skill in research work, and a grave blow to science and engineering must be added to the human loss to their families and colleagues.

Thus grows the long list of those who have given their lives for the increase of human knowledge and welfare.

The Fourth International Congress of Chemistry

Abstract of the Minutes of the Cambridge Meeting

By Jean Gérard, General Secretary

THE Fourth International Congress of Chemistry was held in Cambridge, June 17 to 20, 1923. Sir William Pope, president of the Union of Pure and Applied Chemistry and professor of chemistry of the University of Cambridge, presided. The program included meetings of the council, a meeting of the general assembly, and committee meetings.

The council met the day after an extremely cordial reception by the British Federal Council for Pure and Applied Chemistry, in the Arts School, to take up the question of new admissions and to lay out the program of the general assembly.

The admission of Brazil, whose government had applied for membership in the Union, was unanimously carried. The president of the conference brought out the point that the International Research Council does not allow its subsidiary international unions to accept new member-countries without these countries being first admitted to the International Research Council. The countries who desire to be admitted to the Union must therefore send a request for admission to the International Research Council and mention therein their desire to be admitted to the International Union of Pure and Applied Chemistry.

The general assembly at its subsequent meeting approved the report of the president on the acts of the council as well as the report of the auditor on the accounts for the fiscal year just closed, and approved the budget for the present year.

The second part of the meeting was devoted to the assignment of work among the different committees. These committees, after having duly met, submitted for the approval of the council, resolutions, of which a resumé follows.

I. The Committee for the Reform of the Nomenclature of Inorganic Chemistry proposed that the work in the future be placed in the hands of the editors of the principal journals, and especially those of the *Journal of the Chemical Society*, *Chemical Abstracts*, *Gazzetta chimica italiana*, *Helvetica Chimica Acta*, *Recueil des travaux chimiques des Pays-Bas*, and the *Bulletin de la société chimique de France*.

Each country is to send its suggestions to these various publications, which will be duly qualified to submit them for general discussion. It is the opinion of the committee that when nearly unanimous agreement has been reached methods could be devised to insure the adoption of the conclusions so that these could serve as a basis for new proposals.

The committee deems it necessary that reports, even if not complete, be sent to the central organ as soon as possible.

The decisions enumerated below must therefore be considered purely provisional:

1—Regarding the unification of chemical symbols proposed for Formula Index, the committee has not deemed it wise to insist immediately on its own authority on the acceptance of definite symbols for glucinium (Gl), beryllium (Be), niobium (Nb), or columbium (Cb). The committee feels, however, that next year a final decision must be reached, after due consultation of the nations represented. There are two points to be considered—the original names and the original symbols. Other points may be brought up for consideration. The decision on these questions, which must be reached before January of next year, will be communicated to the delegates who will sit at the next session.

2—The committee feels that the writing of formulas of acids, bases, and salts in each country should conform to the usual custom in any particular language—that is, in the countries of Anglo-Saxon languages one would write HCl, H_2SO_4, $BaCl_2$, Na_2SO_4, $Ba(OH)_2$, etc., whereas in the countries of Latin languages one would write ClH, SO^4H^2, SO^4Na^2, $BaCl^2$, $(OH)^2Ba$, but in the same language one should not write sometimes $ClNa$ and sometimes $NaCl$, nor sometimes SO^4Na^2 and sometimes Na_2SO_4.

3—The word "hydrate" will be reserved for combinations containing H_2O—like the hydrate of chlorine, $Cl_2.rH_2O$; the hydrate of sodium sulfate, Na_2SO_4, $10H_2O$. The word "hydroxide" will be reserved for chemical combinations containing OH—aluminium hydroxide, $Al(HO)_3$; barium hydroxide, $Ba(OH)_2$.

4—The committee accepts the names of acids as given in the French report when these agree with those in the Danish and American reports.

To the accepted list may be added chromic acid, H_2CrO_4; molybdic acid, H_2MoO_4; manganic acid, H_2MnO_4; and permanganic acid, $HMnO_4$.

Those parts of the report which do not agree will form the subject of subsequent discussion—for example, hyposulfite (hydrosulfite in French), pyrosulfuric acid, heptamolybdic acids, etc.

Condensed acids, like pyrosulfuric, heptamolybdic, etc., will be fully discussed later, but the committee feels that the suggestion submitted in the Spanish report to designate such acids by the prefix "anhydro," preceded by a numerical index and followed by the specific name of the acid with a numerical prefix, could be adopted as a basis for discussion—for example, chromic acid, H_2CrO_4, *di*anhydro-*tri*chromate $K_2Cr_3O_{10}$; iodic acid, HIO_3; *di*anhydro-*tetra*iodate, $M_2I_4O_{11}$, etc.

It might be possible for certain acids which stand out above the others on account of the large number of their derivatives, to preserve their names—as, for example, heptamolybdic acid, which applies exclusively to the hexacid $H_6Mo_7O_{24}$.

5—The acid salts will be named in accordance with the French report—for example, $CaHPO_4$, calcium acid phosphate; KH_2PO_4, dihydrogen potassium phosphate.

6—The degree of valence of metals in spoken language would be expressed as given by the French report without inconvenience for any country. This would end all the discussion on the terminations *-ous*, *-ic*, *-a*, *-o*, etc., which have been proposed various times.

7—The nomenclature of complex compounds on which a report has already been laid before the second congress ought to be taken up.

II. The Committee for the Reform of Nomenclature in Organic Chemistry presented the following resolutions:

1—The committee, organized at the Lyons congress and consisting of the editors of the *Journal of the Chemical Society*, *Chemical Abstracts*, and *Bulletin de la société chimique de France*, will be increased to six members by adding to it the editors of the *Gazetta chimica italiana*, *Helvetica Chimica Acta*, and of *Recueil des travaux chimiques des Pays-Bas*. These publications may designate a representative.

2—The question of nomenclature under discussion will be submitted to this committee of six. The suggestions emanating from individuals or national committees or committees of chemical societies, will be submitted to this committee.

The decisions of the Committee of Six must be unanimous. They will be submitted for approval at a meeting of the Union.

3—The Geneva nomenclature will be taken as basis for new discussions, and this resolution will be transmitted to the Committee of Six.

4—The Committee of Six may hold a special meeting for the purpose of exchanging opinions and facilitating subsequent work.

III. The Committee on the Reform of the Nomenclature of Biological Chemistry adopted the following resolutions dealing with the most general names:

1—The name of a new compound, the chemical constituent of which is known, must be made up in accordance with rules of nomenclature of organic chemistry.

2—The word "glucid" will be used to designate the group of substances which comprises the simple reducing sugars and substances which give one or several of these sugars by hydrolysis.

3—The word "lipoid" will no longer be used.

4—The word "lipide" will designate the group of substances which comprises the fat bodies and esters which possess analogous properties (lecithines, phosphatines, etc.).

5—The word "protide" will designate the group of substances which comprises the natural amino acids and substances which by hydrolysis give one or more of these acids.

IV. The Committee on Bibliography passed the following resolutions:

1—That the secretary of the Union make an investigation of the bureaus of documentation existing at the present time and publish a list of these bureaus with their addresses, their specialties, and a short description of their organization.

2—That the bureaus of documentation unify as much as possible their methods of work in accordance with the principles adopted by the International Institute of Bibliography and the Subcommittee on Bibliography of the League of Nations.

3—That the Union finance the printing of classification tables, standardized in their present form and provisionally revised, in order that these tables can be submitted to the critical review of competent experts in various countries.

4—That each country make a list of the journals directly interested in pure and applied chemistry and that these lists be brought together and distributed by the general secretary of the Union.

5—That, in view of the resolution of the Subcommittee on Bibliography of the League of Nations, chemical publications send at least two copies, and preferably five copies, of their annual index to the International Institute of Bibliography in order that this institute may be in a position to draw up the Central Annual Bibliographical Index of Authors' Names.

6—That the general secretary of the Union make every possible effort to persuade those publications which have not yet come to a decision to conform with the two following resolutions which were passed at the previous Congress:

(1) That all original papers in chemistry have the address of the author or that of the laboratory where the work was carried out.

(2) That the journals give a resumé of their articles in one of the languages accepted by the editorial board of the Annual Tables of Constants, in such a form that it could be published in an abstract journal.

V. The Committee on Physico-Chemical Standards passed the following resolutions:

1—That the committee approves the financial report of the Bureau of Physico-Chemical Standards for the fiscal year 1922–1923.

2—That it is the desire of the committee that the Bureau of Physico-Chemical Standards investigate, through circular letters addressed to the directors of the research laboratories, what are the new physico-chemical standards, the preparation of which would be most urgent. The results of such an investigation will facilitate coördinating the work of the bureau.

3—That in the opinion of the committee it will be well to ask the Bureau of Physico-Chemical Standards to study the possibilities of obtaining the coöperation of certain chemical firms specializing in the manufacture of pure products, and to submit to the next congress a plan to obtain such a coöperation.

4—That the committee congratulates Mr. Timmermans, secretary of the Bureau of Physico-Chemical Standards, on the fruitful and extensive work that he has carried out with remarkable devotion. The committee hopes that he may continue the publication of the critical tables of physico-chemical constants of organic compounds, this work being considered by the committee of an importance which could not be exaggerated.

5—That the committee would like to see a closer coöperation between the Bureau of Physico-Chemical Standards and the Committee on Pure Products for Research.

6—That the committee recommend to the council for the fiscal year 1923–1924 a supplementary appropriation of 15,000 francs.

VI. The Committee on Pure Products for Research, in answer to the question asked by the International Oceanographic Association of the Mediterranean, replies that pure sodium chloride may replace standard sea water for the volumetric determinations actually in use in oceanographic work.

In addition the committee passed the following resolutions:

1—That the list of pure products for analytical work be not made up until after the various countries represented on the committee have an opportunity to discuss the matter with their analytical chemists. Nevertheless, in order to avoid too long a delay in the carrying out of the work of the committee, the list of reagents enumerated in the index (Types of the Congress of 1922) will be temporarily adopted, this list being subject to further revision.

2—That the committee instruct its members to organize during the months following the meeting, and to distribute among the various members of the committee, or among the various competent persons designated by the committee, the experimental work necessary to complete the international list of pure products for analytical work.

3—That it is the desire of the committee that its president put himself in contact with the members of the Bureau of Physico-Chemical Standards with a view to finding a means to prevent the same reagent from being classified in one case as a pure product for analysis and in another case as a physico-chemical standard.

VII. The Committee on the Bibliography of Industrial and Technological Products desires that the bibliographical work on raw materials and industrial products, such as has been begun by the central office, be pushed along as actively as possible in every state represented in the Union, even though the number of manufacturers coöperating be small.

The committee requests that the Bureau of Vegetable Raw Materials, which is actually working in France, be incorporated in the Bibliographic Bureau of Industrial and Technological Products. The above-mentioned bureau is directed and subsidized by the French Parliament as well as by interested manufacturers. Its object is to complete the official work of the university in bringing together all information on the origin and quality of French and foreign drugs known in the market.

The committee requests that the Musée de la Faculté de Pharmacie de Paris and the Laboratoire Central d'Etudes et d'Analyses des Produits Médicamenteux et Hygiéniques (Laboratoire de la Commission du Codex) be incorporated in the central office. With the help of these three organizations it will be possible to bring together the bibliography concerning vegetable raw materials utilized in chemical industry in the manufacture of drugs and perfumery. The name of these united bureaus shall be "Service de Documentation sur les Matières Premières et les Produits Industriels" (Bureau of Bibliography of Raw Materials and Industrial Products).

VIII. The Committee on the Choice of a Thermochemical Standard took note of the decision reached by the Bureau of Standards, Washington, that the benzoic acid prepared by this bureau cannot be obtained as standard substance for calorimetric determinations except for purely scientific purposes, and that it becomes therefore necessary to employ for technical purposes, in the determination of heats of combustion of solid and liquid fuels, benzoic acid from other sources.

The committee recommends, nevertheless, that the standardizing of calorimetric bombs be carried out by the use of samples of benzoic acid which have been duly approved by a competent thermochemist. The committee will eventually take up the question of drawing up necessary instructions for the approval of such samples.

The committee deems it necessary that, in converting thermochemical data determined in calories into absolute units, and vice versa, use should be made of the conversion factor: 1 calorie 15° C. = 1184 joules, the average value accepted at the present time, in accordance with the decisions reached in 1923 by the International Critical Tables, following the advice of several scientific societies.

IX. The Committee on the Tables of Constants unanimously passed the following resolutions:

1—That the Union approve the financial report submitted by the Committee on the Annual Tables of International Constants of Chemistry, Physics, and Technology for the fiscal year 1922, and that this report be transmitted to the International Research Council.

2—That the attention of the Union be called to the fact that the following countries have contributed to the International Fund created in 1922: Belgium, Denmark, Spain, the United States, Great Britain, France, Italy, Norway, the Netherlands, Portugal, Switzerland, and Czecho-Slovakia.

Concerning those countries which do not appear on the above list but whose contribution may be considered as practically certain the Union should pass a resolution to the effect that this should be made with the least possible delay.

3—That the Union should take cognizance of the final organization of the International Fund, the necessity for which had been recognized in Lyons in 1922, and signify its appreciation of the value of the annual international tables as a bibliographic publication indispensable to scientific and technical progress.

4—That the Union should pass a resolution recommending that the numerical bibliography of the years 1917–1922 be published as rapidly as possible in order that the International Tables of Constants and Numerical Data resume as soon as possible its annual publication.

The committee hopes that it will be possible for the committee on the tables to carry out its plans with the help of the annual subscription open for that purpose under the patronage of scientific and industrial societies of the adhering countries.

Regarding physico-chemical symbols, the committee includes the following modifications:

1—The second part of the list of symbols should have for its title "General Constants" instead of "Universal Constants."

2—In the third part, ninth line, "molar fraction" should be substituted for "mol fraction."

3—Page 305, fifth part, second line, the symbol n in the column "Alternative Symbols" should be omitted.

4—Fifth part, eighth line, replace $M(\alpha)$ by M as a symbol for molecular rotatory power.

5—Fifth part, last line, replace $M(\omega)$ by (Ω) as a symbol for molecular rotation.

6—Page 506, third line from bottom of page, suppress the words "Soschmidts Numbers."

7—Page 509, in paragraph headed "Entropy," second line, suppress the words "on the ground that this symbol was used by Willard Gibbs, and also***"

8—Page 511, in accordance with general custom the molecular rotation is defined by the relation

$$M = \frac{M \times (\alpha)}{100}$$

The employment of ω for the specific magnetic rotation and Ω for molecular magnetic rotation is recommended; the molecular magnetic rotation is defined by the relation

$$\Omega = \frac{M \times (\omega)}{15}$$

In the alphabetical list these changes should be taken into account.

The committee proposes to appoint a subcommittee for the purpose of bringing together the suggestions leading to additions or changes in the list of symbols and to put forth proposals. This committee will be headed by Professor Cohen and will include Messrs. Findley, Marie, and an American member to be appointed by the National Research Council of the United States.

X. The Committee on Solid Fuels decided to complete the work undertaken in the countries adhering to the Union on the nomenclature of solid fuels, as well as on the methods of determining their essential characteristics, especially the volatile content, the calorific power, and the agglutinating power. The committee insists that the answers should reach the general secretary before January, 1925.

XI. The Committee on Liquid Fuels decided to extend the work undertaken on the nomenclature of different groups of liquid fuels as follows: petroleum and its derivatives; distillation products of coal, lignite, peat, wood and bituminous shales; alcohol; vegetable oils.

The committee requests that answers reach the general secretary before January 1, 1925.

XII. The Committee on the Study of Ceramic Products passed the following resolutions:

1—That the Union recommend that from a technical and scientific point of view the term "ceramic" be employed for all industries manufacturing the following products:

(*a*) All kinds of burned clay products, such as stoneware, earthenware, brick, tile, sewer pipe, terra cotta, china, porcelain, etc.

(*b*) Cementing materials, such as portland cement and dental cement; lime, plaster, and a variety of magnesia and gypsum products whose constituents are of an earthy nature and which, after a preliminary treatment which involves a calcination, acquire the property of "setting" to a greater or less extent, when mixed with the proper liquids.

(*c*) All varieties of glass and glassware, including quartz glass, glazes, enamels, and many of the artificial precious stones.

(*d*) Enameled metal products, where the enamel itself is a ceramic material applied to the metal at high temperature, the metal serving only as a skeleton to give the desired form and strength to the glass which it supports.

(*e*) Refractory articles or materials, either wholly or partially composed of or manufactured from clay, silica (in its various forms), alumina (bauxite), magnesia (magnesite), lime, chromite, asbestos, zirconia, mica, the rare earths, certain carbides and nitrides, and in general any nonmetallic product capable of withstanding elevated temperatures. In all products of this class it is evident that a high temperature treatment is fundamental.

(*f*) Abrasive materials such as carborundum, alundum, and zirconia (and by association, finely divided silica and emery), together with the products manufactured from them by bonding with an earthy material.

(*g*) Various electrical and thermal insulating products in the manufacture of which earthy materials enter as an important element.

2—The committee recommends that in each country an exact nomenclature of raw materials and manufactured products of the ceramic industry be instituted together with their chief characteristics.

3—The committee proposes unanimously that the question of the choice of standards of various earths to be used in the study of chemical and physical properties of refractory materials, as well as the proposed methods of studying such properties, be included in the program of the next congress.

4—On the proposal of M. Henry LeChatelier and M. Capsa, members of the committee, the committee believes that the proposed work ought to be done by various laboratories in all countries, and it hopes that this work will be carried out with the same raw materials in order to reach comparable conclusions.

It is the opinion of the committee that it will be desirable to agree on the form of apparatus to be employed for the determination of dilatation coefficients.

5—The committee hopes that M. Henry LeChatelier will be willing to undertake the direction of the necessary researches and look after their proper coördination.

XIII. The Committee on Food Preservation passed the following resolutions:

1—That as soon as possible the various countries belonging to the Union, who have not yet appointed a delegate, do so in order that the membership of the committee be completed.

2—That the subcommittee of five members composed of Messrs. Alsberg, Bordas, Paterno, Pondal, Voerman, present at the next congress a general report on the bibliography which has been gathered up to the present, and which could be assembled from now until then, in regard to all matters relating to food legislation in the various countries.

3—That at the time of the next congress the delegates of the various countries, taking into consideration the legislation in force at the time, present their conclusions as to the effects of employing the following products as food preservatives: benzoic acid, boric acid, salicylic acid, sulfurous acid, sulfates and formaldehyde, for the purpose of undertaking a systematical and physiological investigation on the possibility of using chemical products in food preservation.

4—That the chemists of all nations submit opinions concerning the chemical processes of food preservation, in order that steps tending towards uniform legislation founded on experimental basis be initiated.

5—That the coöperation of the "Laboratoire International d'Analyse des Matières Destinées à l'Alimentation des Hommes et des Animaux" be requested for the researches to be undertaken.

XIV. The Committee on Scientific and Industrial Ownership presented the following resolutions:

1—The committee, considering that in the Latin group, which is composed of countries granting patents without examination, the unification of legislation appears to be more capable of realization than in the others, invites these countries to get together as soon as possible with the idea of forming the first group with uniform legislation.

2—Considering that the original purpose toward which one must work should be to permit research workers to protect their discoveries, and considering that on the other hand research workers cannot carry out their researches in secret, but must on the contrary, be able to publish the results of their work as they are obtained, the committee resolved:

That it is inadmissible that one should oppose to the holder or the applicant of a patent the results of his own work for a certain period of time after it has been published.

3—The committee declares that a purely scientific discovery should be legally protected.

4—A proper definition of this new legal right will be studied by the committee.

5—In order to secure the coördination of all efforts the president of the committee is appointed as a delegate to the Committee on Intellectual Coöperation of the League of Nations and to the International Chamber of Commerce to present and uphold the views of the committee.

XV. The Committee on Industrial Hygiene passed the following resolutions:

1—All the reports submitted on the question of dusts should be printed and distributed, as they contain matters of great interest which it would be most important to disseminate.

2—The committee requests the Council of the International Union to give a prize for the best published essay on smokes, gases, fogs, and noxious vapors to be met with in manufacturing, their elimination, and the protection against their effects. The essays submitted should be general and descriptive in character, should include the latest progress in their particular subject, and should be within the reach of the general reading public.

The council of the Union should undertake their distribution.

The committee requests that the council of the Union establish a prize to be given to the inventor of an apparatus of recent construction for the suppression of smoke. In case no recent inventor could be found the prize should be given to that person who had done the greatest amount of work and obtained the best results on the problem of the suppression of smoke.

The committee requests that the council communicate with all chemists specializing in this particular branch in order to obtain from them their scientific results on this matter, and that they also furnish exact data on (*a*) the noxious effects produced on the workmen and the neighboring communities by certain emanations, and (*b*) the means employed to suppress them.

3—The committee requests that each nation send to the next congress a complete report on the legislation concerning industrial hygiene in its own territory. This report should include the legal matters covering differences of work and those covering the suppression of nuisances to neighboring communities. Each country should communicate to the general secretary a list of the administrative organizations charged with the drafting and enforcement of laws and regulations concerning industrial hygiene.

4—The committee requests that its president collect information on the following subjects:

(*a*) Methods of analysis employed in the determination of the quantity of hydrofluoric acid present in the smokes and vapors where it is likely to be found, especially in superphosphate manufacture.

(*b*) Determination of the minimum value of acidity in smokes when these have been discharged. This figure is fixed in Germany at 5 grams per cubic meter, in England at 8 grams per cubic meter, and in Italy at 6 grams per cubic meter, expressed in SO_2. The committee recommends that it would be wise to agree on a figure acceptable to all, and that it would be well to obtain agreement on the method of determination and on the method of expressing this figure.

(*c*) The possibility of suppressing offensive odors in industry when these are due to more or less unknown products which cannot be condensed, as, for example, in sewage disposal, slaughter houses, etc.

5—The committee requests that at the next congress a report be made on all methods and apparatus intended to combat incipient intoxication from poisonous gases in factories.

6—The bibliography and the resolutions of the committee should be communicated to the Bureau of Hygiene of the League of Nations and to the International Labor Bureau.

XVI. The Committee on Finance passed the following resolutions:

1—The committee, after having examined all the requests for appropriations made by the various committees, records that owing to the present state of the finances of the Union it cannot grant all the requests that have been made.

2—As a supplementary appropriation, after having studied the difficult financial situation faced by the Bureau of Physico-Chemical Standards, it decided to grant to this committee for the period extending from April, 1922, to November, 1924, the sum of 7500 frances, instead of 15,000 francs as requested.

The Committee on Finance finds itself restrained by the principle that the contributions from the countries belonging to the Union are essentially intended for the administrative expenses of the Union. The committee requests that the various committees should address themselves to the general secretary for all matters concerning correspondence and printing.

All these conclusions and resolutions were unanimously adopted by the council of the International Union at its meeting of June 20.

In order to expedite the work of the Union and to insure the continuity of it during the space intervening between the two meetings, the council requested the executive committee to ask the member of each permanent committee to appoint by correspondence a president to serve until 1925—that is, for the same period as the members of the present committees.

Following the decision to increase the number of vice presidents of the Union to six, th. council nominated by acclamation two new vice presidents, E. Cohen (Netherlands) and Dr. Sakurai (Japan).

The council adjourned after having chosen Copenhagen as the place of meeting for the Fifth Congress of the International Union of Pure and Applied Chemistry.

All these decisions were placed before the delegations at the closing meeting of the general assembly.

The congress decided in closing to create a committee to coöperate with those organizations which undertake to exchange students and professors between the universities of the various countries with the idea of bringing about such exchanges among professors of chemistry.

Meeting of Missouri Section

The Missouri Section of the AMERICAN CHEMICAL SOCIETY started its year's work on the evening of September 20. Dr. Philip A. Shaffer, professor of biological chemistry from the Medical School, Washington University, St. Louis, was the speaker of the evening. His topic was "Insulin, Its Properties and Methods of Preparation." Dr. Shaffer has done much toward the improvement of the methods of separation of this remarkable substance, and his talk on the disease diabetes and its relief by this substance was very enlightening to the many who were present. The meeting was the largest that has been held for some time; the fact that the audience was made up of people of widely scattered interests seemed an indication that there is a need that the local section can fill in bringing speakers here.

New Chemistry Building at Missouri

Following its plans for the expansion of the Chemistry Department, the University of Missouri is just completing a new building for the chemical work. This building is the third building on the campus to be devoted entirely to chemistry. There will be an auditorium seating 175 students, and laboratory locker space for 600 students. There are five small research laboratories for instructors, besides administration offices and storerooms. The attic has been finished off into four rooms and will probably be used as research laboratories for graduate students.

Denatured Alcohol Production

PRODUCED, USED, REMOVED, OR DUMPED, AS INDICATED BELOW, FOR THE

	Denatured Alcohol Produced					Removed from Denaturing Bonded Warehouses	Alcohol and Denaturants Dumped	
Formulas	1907	1908	1909	1910	1911	1912	1913	1914
Completely Denatured Alcohol								
1							4,961,105.20	4,932,494.32
2							261,135.58	280,635.24
3								
4								
5								
9								
Total C. D. A.		1,812,122.38	2,370,839.70	3,076,924.55	3,374,019.92	4,229,741.67	5,222,240.78	5,213,129.56
Specially Denatured Alcohol								
		Denatured Alcohol Used				Alcohol and Denaturants Dumped		
1		768,476.63	1,258,120.07			2,493,630.86	2,839,020.80	3,055,817.33
2		60,144.07	65,141.77			49,665.00	75,517.40	69,135.94
2-A		35,097.24	110,460.49			172,723.20	201,468.80	162,091.61
2-B								45,928.13
3		63,520.68	36,422.04			8,638.37	9,229.55	3,039.42
3-A							59,165.43	225,813.65
3-B								
4		288,981.36	365,590.06			403,943.91	511,329.65	564,010.34
4-A								
5		524.11	5,978.45			5,922.51	5,579.10	6,310.71
6		31,946.49	4,077.90					
6-A			16,730.77			194,869.32	229,014.73	245,755.56
6-B								
7		186.39						
8		190.19	1,069.95			742.40	989.70	804.40
9		3,930.48				3,992.96		
10			233.53					15,206.45
11		332.95	1,198.84			1,339.15	1,049.96	912.06
12		34,129.43	39,387.41			20,099.87		
12-A						5,344.70	15,456.31	11,122.47
13								
13-A		211,495.49	266,846.70			377,993.71	471,110.53	599,634.61
14		264.16	1,171.81			1,770.80	1,660.28	2,426.54
15		1,582.34	6,916.42			5,781.26	5,567.98	6,690.46
16		554.44	4,089.84			5,338.00	5,634.70	5,053.27
17			1,661.54			8,454.36	9,585.54	8,259.80
18						172,596.06	166,890.26	160,692.86
19						400.00	47.04	3,140.42
19-A								
20								
Total S. D. A.		1,501,356.45	2,185,097.59	3,002,102.55	3,507,109.94	3,933,246.44	4,608,417.76	5,191,846.03

TAX-FREE denatured alcohol was first produced in the United States under the Act of June 7, 1906, "for use in the arts and industries and for fuel, light, and power." Supplemental laws were later enacted, with the result that the manufacture and use of that product soon became a vital factor in the commercial life of the nation, and was recognized as a "key" industry during the World War.

The advent of prohibition presented an added, and perhaps more potent, reason why pure ethyl alcohol should be replaced as far as possible with tax-free denatured alcohol, and Section 10, Title 3, of the National Prohibition Act provided for denaturing plants at which ethyl alcohol could be lawfully denatured "by the admixture of such denaturing materials as shall render the alcohol or any compound in which it is authorized to be used unfit for use as an intoxicating beverage." To date, however, the Government has not extended the use of tax-free denatured alcohol to the production of pharmaceuticals or other commodities, intended for "internal" consumption, however unfit the final product may be for use as an intoxicating beverage. It is thought that this attitude with respect to "internal" medicines, etc., is more a question of administrative policy than law, and that eventually the Government will recede from its position in the interest of legitimate chemical development.

As indicating the progress of the denatured alcohol industry from humble beginnings to its present large proportions, we publish this table compiled by the office of James P. McGovern, the Washington attorney of the U. S. Industrial Alcohol Company. Although the columns for the years covered are variously headed, "Denatured Alcohol Produced," "Removed from Denaturing Bonded Warehouses," "Denatured Alcohol Used," "Withdrawn from Denaturing Plants," etc., as they appear in the Annual Reports of the Commissioner of Internal Revenue, the tabulation is to be regarded in its entirety as conveying a fairly comprehensive idea of the amounts, *by formulas*, of both completely and specially denatured alcohol *produced and used* during the fiscal years involved. It is regretted that it was not possible to have the compilation complete in all respects. The reason for the omissions will be found in the "Note," page 1087. The figures for the fiscal year ending June 30, 1923, are not yet available.

Space does not permit the listing of the innumerable uses for which denatured alcohol has been authorized. It is sufficient to say that specially denatured alcohol, Formula 1, alone has been prescribed for over two hundred and fifty items. Any one interested in such uses, however, may find the composition of the formulas and their respective uses fully set forth in the Appendix to Regulations No. 61 of the Internal Revenue Bureau, published September, 1922, under the title "Formulas for Completely and Specially Denatured Alcohol." Copies of such appendix may be had by addressing the Industrial Alcohol and Chemical Division, Internal Revenue Bureau, Washington, D. C.

In studying the table it should be noted that more than half of the formulas have come into existence since the World War, and most of these since prohibition. While the total amounts for each of the fiscal years ending June 30, 1916, 1917, 1918, and 1919, respectively, exceed those for 1920, 1921, and 1922, the difference may be largely attributed to the tremendous withdrawals of Specially Denatured Alcohol, Formula 2-B, for the manufacture of smokeless powder, trinitrotoluene and other war materials, and a comparison of the totals of the years shown (excluding the war years) will reveal with greater accuracy the normal but rapid growth of this husky industrial infant.

Denatured Alcohol Production *(Concluded)*

FISCAL YEARS SHOWN, ENDING JUNE 30, RESPECTIVELY. (QUANTITIES IN WINE GALLONS)

	Alcohol Denatured under Various Formulas			Removed from Denaturing Bonded Warehouses			Withdrawn from Denaturing Plants	
Formulas	1915	1916	1917	1918	1919	1920	1921	1922
				Completely Denatured Alcohol				
1	5,149,410.88	7,184,620.75	9,140,999.26	8,313,416.96	7,180,520.30	6,926,825.22	50,420.00	166,215.87
2	237,236.08	687,332.07	1,367,920.08	1,974,904.37	2,806,520.76	2,451,144.07	251,201.30	300,191.79
3						28,323.97	50,042.82	117,370.94
4					1,433.11	390,558.01	268,315.34	22,595.75
5						3,679,944.90	6,496,719.23	9,843,651.33
6							5,109,820.18	5,759,877.15
Total C. D. A.	5,386,646.96	7,871,952.82	10,508.919.34	10,288,321.33	9,988,566.17	13,476,796.17	12,226,518.87	16,209,902.83
				Specially Denatured Alcohol				
1	3,026,030.54	4,504,202.02	4,685,613.19	4,228,493.16	4,402,655.07	6,563,351.12	3,993,825.77	4,994,240.74
2	80,547.02	421,849.00	176,655.65	214,055.88	88,553.44	112,518.66	64,722.63	
2-A	201,488.86	319,462.86	69,444.70	65,747.48	36,517.62	115,548.56	38,770.01	72,731.38
2-B	3,357,154.38	27,855,774.23	28,551,736.36	27,843,909.08	16,275,674.09	2,331,322.09	1,990,326.16	2,450,939.20
3	398.50	3,944.82	5,767.84				548.01	35.02
3-A	224,891.50	274,945.74	230,455.28	222,993.33	214,441.89	344,279.89	229,908.85	540,770.88
3-B	339.07	172.70	723.28	14,807.66	21,398.68	7,515.06	10,370.82	8,493.23
4	582,258.48	664,787.04	868,065.29	904,023.33	745,704.61	871,198.39	679,547.60	898,947.81
4-A								
5	5,617.41	7,228.91	6,581.46	5,532.29	7,277.08	41,463.68	5,763.75	8,193.93
6								3,272.64
6-A	238,961.22	456,091.25	318,679.45	444,355.77	804,780.71	86,850.35	99,318.44	67,107.65
6-B	525.53	409.00	5,039.00	5,739.92	11,793.75	13,671.67	5,829.06	8,084.42
7								
8	1,173.67	1,124.40	504.98		5,205.04	1,564.41		4.85
9	46.30	112.10	7,561.66	3,528.91	5,747.41	11,748.82	2,385.33	5.04
10	15,167.82	49,700.81	125,528.97	154,149.84	309,940.21	854,610.34	73,801.31	5,559.29
11	1,313.00	851.60	1,441.65	923.10	735.86	990.20	781.16	651.92
12					2,974.79	12,933.49		
12-A	24,301.90	53,992.66	97,706.05	88,004.66	83,316.84	153,324.61	141,877.53	281,093.04
13								5.00
13-A	606,891.20	888,915.92	981,284.73	1,042,072.48	1,009,774.31	1,309,239.99	966,048.04	1,780,771.06
14	2,917.11	2,613.48	4,378.02	6,363.93	695.05	1,894.25	1,226.77	1,636.50
15	7,089.57	6,103.43	12,652.19	9,768.17	31,774.63	104,476.45	14,510.96	8,220.81
16	5,528.67	9,235.51	23,361.92	25,902.30	28,789.39	24,810.34	3,705.93	9,156.90
17	13,087.09	95,164.40	25,759.96	28,052.79	65,109.64	57,436.82	49,132.69	13,598.38
18	199,723.84	240,912.30	233,462.12	473,869.35	950,941.33	1,160,120.01	725,816.56	1,036,893.33
19	4,369.13	104,426.82	24,086.84	27,410.61	26,875.13	54,281.85	42,392.80	42,537.95
19-A								
20		12,415.40		69,810.43	66,783.20	13,775.94	12,445.70	13,034.83
21		2,832,717.16	8,656,805.58	3,608,711.26	2,913,700.00	405,826.96	65,100.00	1.00
22			7,689.07	3,920.65	2,945.30	40,032.39	50,340.73	7,608.61
23			16,857.87	20,739.18	19,029.62	22,514.21	58,271.04	23,446.05
23-A							137,517.65	466,831.61
23-B							262.27	1,073.24
23-C							1,467.21	5,739.20
23-D								986.44
23-E								
23-F								
24			17,177.00	8,818.22		24.52	640.49	1,308.44
25			11,311.13	121,384.48	88,104.27	131,787.53	112,491.18	149,191.99
26			2,100.28	14,111.28	23,001.28	75,404.84	9,340.16	4,962.55
27			2,246.77	49,970.95	20,799.88	54,988.28	37,797.87	48,758.10
27-A						885.05	7,785.44	9,706.92
27-B								5,395.18
28					26,399.34	197,290.50	123,477.92	74,054.75
28-A								
29						18,161.12		24,677.07
30					426.67	19,533.33	10,896.83	15,873.61
31					750.78	2,933.21	427.52	92.43
31-A						33,625.90	33,816.70	49,651.87
31-B						243.00	16,573.14	22,366.93
31-C							100.32	45.26
32						14,078.34		11.00
33						2,085.53	2,360.63	4,171.55
33-A								3,621.06
34							4,658.40	9,204.84
35								8,768.44
35-A								99,360.55
36							447.41	197,996.68
37							24,052.87	330,416.20
37-A								
38							962.74	6,555.72
38-A							404.18	2,315.08
38-B								690.93
38-C								
38-D								1,039.64
38-E								467.14
39							38 656.42	175,189.30
39-A							50,057.95	1,330,091.32
39-B								1,425,542.59
39-C								
39-D								
40							26,357.33	321,975.38
41								1,061.57
42								1,975.71
43								214.99
44								9,282.56
45								1,549.24
46								5.00
47								
Experimental					1,017.03	497.55		
Total S. D. A.	8,599,821.81	38,807,153.56	45,170,678.29	39,707,170.49	28,293,615.94	15,268,839.25	9,967,320.28	17,089,263.54

NOTE: Compiled from the Annual Reports of the Commissioner of Internal Revenue. Amounts for 1907, amounts by formulas of *Completely* Denatured Alcohol for 1908, 1909, 1910, 1911, and 1912, and amounts by formulas of *Specially* Denatured Acohol for 1910 and 1911 are not given in such reports and are not available.

AMERICAN CONTEMPORARIES

Frank Austin Gooch

IF IT be true, as some claim, that the general atmosphere of Boston is one of cultured manners, no better illustration of the influence of such an atmosphere could be selected than the subject of this sketch. No one who has ever come in contact with Professor Gooch can fail to carry away the impression that he has met a man of peculiar charm of manner. Born in Watertown, Mass., of parents belonging to families connected with the early history of the country and representing the highest type of culture, his early life was spent in the vicinity of Boston. His father was a prominent lumber merchant in Cambridge, and at one time chief assessor of that town. His mother was a member of the Coolidge family.

Frank A. Gooch

He entered Harvard at the age of sixteen and was graduated with the class of 1872.

His early inclination was toward medicine, but upon graduation, and until 1875, he carried on chemical and mineralogical studies at Harvard, and at the same time acted as assistant to Prof. Josiah P. Cooke, who was famous in his day as an experimental lecturer. Doubtless Professor Gooch's skill in manipulation and his clearness in description of chemical phenomena, so characteristic of his later work as a teacher, had their origin in this early training.

During the years 1875–6, spent mainly in Vienna, he continued his studies along mineralogical and crystallographic lines at the Imperial Museum, and his fund of reminiscences of that period goes to show that he had the most delightful association with the director and others in authority there. Upon his return he received the degree of Ph.D. from Harvard.

He often speaks of the two years which followed, when he held the position of private assistant to Dr. Wolcott Gibbs, as of special value to him, and frequently quotes a common expression of that renowned chemist, famous in inorganic and analytical research, to the effect that "there is practically nothing which cannot be accomplished by patience and caustic potash."

It was probably during this period that Dr. Gooch developed patience and skill and his love for analytical chemistry. To him chemical analysis has never been what many, profoundly ignorant of the subject, have considered it, blind following of directions, or "cook-book chemistry," a term which has been responsible for much neglect of this great fundamental branch of chemistry. Dr. Gooch's mind, stored with a wealth of observed chemical phenomena, finds the greatest joy in devising new analytical processes and in overcoming the difficulties which to many a chemist have seemed to make an analytical procedure useless.

For ten years following his apprenticeship with Dr. Gibbs, his work gave him ample scope for the perfection of his technic in his chosen field. Analytical work in connection with the United States Tenth Census, 1879–1881, the North Transcontinental Survey, 1881–1884, and the United States Geological Survey, 1884–1886, contributed much in the way of preparation for his work at Yale, which really began with the completion of the Kent Laboratory in 1887. It was during this period that he enjoyed from time to time association with Dr. Rafael Pumpelly, the renowned geologist and explorer, and he often turns with great pleasure to the recital of a variety of experiences connected with field and laboratory work.

It was also during these years that much important work was done, such as the analysis of the waters of Yellowstone Park and the invention of the perforated platinum crucible for filtration. The latter alone has made his name familiar wherever careful analytical work is attempted. Shortly after the first description of this almost indispensable analytical device appeared, a well-known chemist said in an address: "The Gooch crucible is to modern analytical chemistry what the needle gun is to modern warfare." This encomium was doubtless more adequate at the time it was uttered than it would be today, when the needle gun has been surpassed by many other inventions, while the crucible still holds its place among necessary equipment.

In selecting Dr Gooch for a position at Yale the authorities chose wisely and well, for he combines the good qualities of administrator, teacher, and director of research. During a period of over thirty years, for he did not take even a week off during term time, until his retirement in 1918, he was at his post.

No man could have a more loyal group of followers than those who have worked with Professor Gooch. His sympathy and liberality are such that a conference with him always resulted in helpful suggestions and in an adequate supply of material for work when special material was needed. A request for a gram generally resulted in a supply of ten grams. As for crude chemicals, they were an abomination to him, and his associates could hardly persuade him to order them for any kind of work. Despite this policy there was on hand at the end of his administration a considerable balance in money to the laboratory's credit, and a supply of chemicals, some of them unusual, which in view of the immediately following post-war scarcity reminds one of Joseph's store of corn laid up against the Egyptian famine. Loyalty to his friends and associates marked Professor Gooch's years of university activity, as all who have worked with him will testify.

Conservative by nature, he keeps fully informed of the progress of chemical science, but does not without careful consideration turn to newly propounded theories. He has always insisted upon the importance of comprehensive study of chemical phenomena along the lines of descriptive chemistry. His retiring disposition has kept him from gatherings of chemists where his presence would have been much appreciated.

His loyalty to local journals has resulted in giving his published work and possibly that of his students less publicity than might have resulted had these papers appeared in the more widely circulated chemical journals. He finds great pleasure and relaxation in the reading of good fiction and in genealogical research. A recent statement in a prominent New York newspaper to the effect that chemists are as a class fond of cats may be disputed, but certainly the feline race has no better friend than Dr. Gooch, nor one more convinced of its intelligence.

His former pupils always love to call on him when in New Haven and talk over their laboratory days and discuss their current problems. His fund of reminiscence is rich, as is also his collection of good stories, and we all enjoy them both, for together with his keen analytical mind he has a rare sense of humor.

Philip E. Browning

NOTES AND CORRESPONDENCE

Shortening—Its Definition and Measurement

Editor of Industrial and Engineering Chemistry:

The writer has made shortening measurements with the shortometer [This Journal, **3**, 79 (1921)] for the last six years and has only recently checked up these measurements, and in no case can he substantiate the conclusions made in the article by Platt and Fleming [This Journal, **15**, 390 (1923)], entitled "The Action of Shortening in the Light of the Newer Theories of Surface Phenomena."

The following series of all shortening measurements is a fair evaluation of the various fats and oils:

> Lard, which has the greatest shortening power, naturally comes first. Compounds rank next, and they have about the same shortening power if they are made by adding oil to animal stearin or to vegetable stearin—namely, hydrogenated vegetable oil. Butter fat follows next in order. The oils cottonseed, peanut, olive, rapeseed, soy bean, and corn, all have approximately the same shortening value, which is about three-fourths of the value of ordinary lard.
>
> Coconut oil is somewhat lower than the previous group of oils and has about two-thirds of the value of lard. Coconut oil if broken up into olein and stearin fractions shows a value higher than whole coconut oil for stearin, and lower for olein.
>
> The iodine number of the whole oil is about 9, that of the stearin about 4 or 5, and that of the olein about 16 or 18. It is evident in this case that the fat with the higher iodine number has the least shortening value.
>
> A liquid paraffin oil with an iodine number of 0.4 has a shortening value very close to that of coconut oil. A sample of white vaseline had a shortening value fully as good as the ordinary oils, or 75 per cent of that of lard.

A little difficulty is experienced in using liquid paraffin oil in baking because the high temperature of baking causes the oil to smoke appreciably and loss is thereby experienced.

The writer has very definitely shown in his original article that hydrogenation of an oil increases its shortening value. The iodine number is very materially decreased; yet the shortening value has increased, which is also at variance with their theory.

All the figures available on the shortening value of oils and fats show no definite relationship between shortening value and iodine number.

Clarke E. Davis

National Biscuit Company
New York, N. Y.
June 22, 1923

……

Editor of Industrial and Engineering Chemistry:

This criticism seems to be based upon a misunderstanding of the article by Platt and Fleming. For example, Davis says:

> All the figures available on the shortening value of oils and fats show no definite relationship between shortening value and iodine number.

In this statement we can entirely agree with him, for our article states:

> The iodine number as such cannot be taken as an indication of the shortening power from this point of view, since glycerides of linoleic acid containing two double bonds (Iodine No. 173) do not cover any greater surface than glycerides of oleic acid containing but one double bond per molecule (Iodine No. 86). For this reason, other factors being equal, shortenings should be arranged in the order of their percentage of unsaturated glycerides.

Once it is clearly understood that it is the percentage of unsaturated glycerides and not the iodine number that must be considered, it is seen that Davis' shortening values fit in well with the theory which we have advanced.

Considering first oils only, we find that cottonseed, peanut, olive, rape seed, soy bean, and corn oils, all consist principally of unsaturated glycerides with a small percentage of saturated glycerides which varies with different samples of the same oil. We are not surprised, therefore, at Davis' statement that they "all have approximately the same shortening value." Coconut oil, which has a noticeably smaller proportion of unsaturated glycerides, has noticeably less shortening power, while liquid paraffin, with the smallest proportion of unsaturated compounds, is properly at the bottom of the list of oils in shortening power.

We would invite attention also to specific statements in our paper to the effect that many factors influence shortening power. We state:

> Many factors are involved in the action of shortening.*** It is evident that no one property can possibly explain the whole action of shortenings.*** Viscosity evidently plays a part.*** The melting point is also a factor.*** A somewhat related quality is plasticity.*** A fat that will remain plastic throughout the mixing has much greater shortening power than one that is either solid or liquid.

It would seem to be self-evident that these factors would have to be considered in arriving at the shortening power of fats not liquid. It is strictly in line with our theory, however, that lard, etc., containing a considerable percentage of unsaturated compounds, should have greater shortening power than vaseline containing practically none.

On the basis of the statements in our paper it is manifestly impossible to expect the relative shortening power of the "olein" and "stearin" fraction of a shortening to be given simply by their proportion of unsaturated glycerides, as differences in melting point, plasticity, etc., introduce other variables in such a case. The same may be said in comparing the shortening power of a fat before and after hydrogenation.

Davis' findings regarding shortening power are, therefore, not incompatible with our conclusions.

Washington Platt

Merrell-Soule Company
Syracuse, N. Y.
September 14, 1923

Calendar of Meetings

Technical Association of Pulp and Paper Industry—Appleton, Wis., October 25 to 27, 1923.

Association of Official Agricultural Chemists—39th Annual Convention, Washington, D. C., November 19 to 21, 1923.

American Institute of Chemical Engineers—Winter Meeting, Washington, D. C., December 5 to 8, 1923.

WASHINGTON NOTES

Nitrite of Soda Hearing

The Tariff Commission held a hearing on the costs of sodium nitrite in Washington on September 10. Only one witness, C. F. Graff, president and general manager of the American Nitrogen Products Co., Seattle, Washington, appeared before the commission. He argued for a 50 per cent increase in the 3 per cent duty on this product, or an increase from 3 cents to $4^{1}/_{2}$ cents per pound. His application was opposed by counsel for the Norwegian Nitrogen Products Co., New York, N. Y., the American sales agents for the Norwegian product. Mr. Graff stated that his company produced about one-half of the domestic output of sodium nitrite, and that the capacity of all the plants of the United States was sufficient to fully meet the domestic requirements. The Norwegian company presented no cost figures. The hearing was continued until September 26 at which time final arguments will be heard. Meantime, it is believed that ample time will be available for the filing of the necessary briefs.

Since the hearing of September 10 the commission has issued a summary of information in the matter of sodium nitrite. This summary consists of information obtained from the public hearing, from publications, correspondence on file in the Tariff Commission, questionnaires sent to manufacturers, and inspection of books and factories of manufacturers by representatives of the commission, and interviews with persons having personal knowledge of this industry. All information in regard to manufacturing costs of individual firms and other information in the nature of trade secrets of processes has been eliminated from this summary, as required by Section 708 of the Revenue Act of 1916.

Improved Cassina Beverage

George F. Mitchell, supervising tea examiner of the Bureau of Chemistry, has developed a new process for making the beverage cassina which eliminates the former "herbish" taste, to which there was some objection. Mr. Mitchell has recently returned from South Carolina where he has been operating the experimental cassina factory which began work last spring. Those who have sampled a hot or an iced drink made from the new processed leaves are enthusiastic over its qualities as a palatable and refreshing beverage. It has a flavor and a stimulating effect that are believed to be distinct commerical assets.

A flavoring extract has also been prepared from the new processed leaves. This extract has been used by the Department of Agriculture to flavor ice cream and the finished product is said to have met with favor. So concentrated is the extract that one tablespoonful will flavor a gallon of ice cream and only 2 cc. are necessary to flavor a carbonated drink.

One decided advantage of the cassina plant is that all the leaves may be used, since they all contain caffein. Tannin, however, is present in a less degree in cassina than in similar beverages.

Sodatol for Distribution

Eighteen million pounds of sodatol, a surplus war explosive, are to be distributed by the Bureau of Public Roads, United States Department of Agriculture, for road-building and land-clearing purposes. The new supply of explosive is very similar to dynamite and picric acid, 12,000,000 pounds of the latter having already been distributed to road-builders and farmers.

Better Lime

Experiments conducted at the Bureau of Standards have shown a way to improve the manufacture of hydrated lime so that the grade known as "finishing" hydrate is regularly produced instead of the grade known as "masons" hydrate, which because of its lesser plasticity commands a lower price. These tests have shown that plasticity depends not alone upon the colloidal content of the hydrate, but upon the effect on this colloid of the manufacturing process.

It has been found that the drying out can be prevented by letting the freshly made hydrate cool in an atmosphere of steam, while flocculation can be prevented by adding small amounts of a readily soluble calcium salt. A hydrator designed to apply these principles has just been completed for further experiment.

September 18, 1923

Personals

Benjamin Alderson, formerly chemist for the American Bottle Co., Streator, Ill., and since February general factory foreman of the company's Newark, Ohio, plant, has been transferred to the Streator factory and promoted to assistant plant manager.

C. Scott Althouse, president of the Althouse Chemical Co., Reading, Pa., is spending about two months traveling through the industrial districts of England, Scotland, France, and Germany.

S. Henry Ayers, formerly bacteriologist of the dairy division of the Bureau of Animal Industry, Washington, D. C., has been appointed director of research of the Glass Container Association.

L. H. Baekeland, honorary professor of chemical engineering in Columbia University, has been made an officer of the Legion of Honor (French) and of the Order of the Crown of Belgium.

J. P. Bonardi, formerly manager of the Assay and Chemical Department of the Mine & Smelter Supply Co., Denver, Colo., has been promoted to sales manager of the New York office, with headquarters at 42 Broadway.

Walter D. Bouner, who has been absent from the University of Utah during the past year on sabbatical leave, has returned and will resume his duties as professor of chemistry at that university.

S. Caplan, formerly research chemist for the Nucoa Butter Co., Bayonne, N. J., has joined the research staff of the Combustion Utilities Corp., Long Island City, N. Y.

John P. Crabb, a recent graduate of the Massachusetts Institute of Technology, is at present employed in the Gas Division of the U. G. I. Contracting Company of Philadelphia, studying the design of the standard water-gas apparatus of this company.

Ellery K. Files, chemical engineer, who has been connected with the Duratex Corporation for over three years, has been given entire charge of manufacture in the plant in Newark, N. J.

The University of Strasbourg has conferred the title of doctor (honoris causa) on **Simon Flexner** and **Jacques Loeb**, of the Rockefeller Institute of Medical Research, and on **William H. Welch**, of the Johns Hopkins University.

Herbert L. J. Haller, associate chemist, who has been on the staff of the Bureau of Chemistry since 1919 and assigned to the Color Laboratory, has resigned to accept a position with the Rockefeller Institute.

M. E. Holmes has resigned as chemical director of the National Lime Association, and accepted the position of development engineer in charge of research for the U. S. Gypsum Co., 205 W. Monroe St., Chicago, Ill.

Ivar N. Hultman has been appointed chemist in charge of operations at the Kingsport plant of the Tennessee-Eastman Corporation.

M. L. Jackson has accepted a position as research chemist for the Piron Coal Distillation Systems, Inc., Detroit, Mich.

The deaths are announced of **F. Krafft**, professor of chemistry at Heidelberg, aged seventy-one, and **Josef Nevinny**, professor of pharmacology at the University of Innsbruck, aged seventy years.

H. A. Kuhn, who has been chief of the department of toxicology of the Chemical Warfare Service for the past four years, has been detailed to the University of Wisconsin for a year for a special course in toxicology under A. S. Loevenhart.

Rex McDill, who has been spending some time in Cuba in research work on the dehydration of fruits, has returned to Riverview, Fla., to continue his researches.

(*Continued on next page*)

PARIS LETTER

By Charles Lormand, 4 Avenue de l'Observatoire, Paris, France

Sale of Reparations Dyes

In the first month of 1923 the French government seized in the Ruhr, by right of the reparations, an important stock of dyestuffs from Badische, Meister Lucius, and Chemische Fabrik. This stock contained about 7000 tons, and the French government, in agreement with the Belgian government, has just decided to put the stock on sale. It is composed chiefly of indigo and alizarin. Since all these products are already being manufactured in France, the sale for exportation will only be permitted if it does not interfere with French and Belgian producers. The dyestuffs not manufactured in France or Belgium, and existing in the lot seized, will be distributed according to priority among the producers in these countries. This sale will certainly have an effect on the dyestuffs market and may bring about a temporary disturbance.

New Method of Volumetric Analysis

MM. Hackspill and Heeckeren have just perfected an original method of elementary volumetric analysis. The substance is roasted *in vacuo,* at a temperature of 800° to 900° C., in the presence of copper oxide. The nitrogen and carbonic acid are collected with a mercury pump and their volume is measured. The carbonic acid is separated by potash. The water produced in the combustion is first separated from the gaseous mixture by condensation at −80° C., and is then directed, in the vapor state, onto the calcium hydroxide. The hydrogen liberated is recovered and measured. Thus, by a single combustion, are obtained, on substances weighing from 2 to 5 cg., three determinations of nitrogen, carbon, and hydrogen.

Fuels

French chemists seem to be directing their attention just now to the study of fuels. M. Piettre has studied the transformation of the coal in humus. The product of oxidation was reduced by a reaction similar to that which permits the transformation of benzine, first into a nitro compound, and then amine (aniline). The product finally obtained was similar to the humus.

M. Paul Lebeau has undertaken the study of the gas formed by the carbonization of solid fuels. Previously, Picter, of Geneva, examined the liquid products obtained by the distillation of combustible liquids in a vacuum. M. Lebeau's method permits the determination, for temperatures from 100° to 1200° C., increasing by fractions of 100 degrees, of the composition of the gas obtained in heating *in vacuo* anthracite, wood, peat, and lignite. Each of these types of fuels gives, by its increasing decomposition, the gaseous volumes which seem sensibly constant for each of the kinds of fuels studied. The total volume of gas formed is estimated at between 150 and 170 cubic meters per ton for the wood, 266 cubic meters for the peat, 228 to 240 cubic meters for the lignite, and 257 to 309 cubic meters for the anthracite.

The analysis of the gas liberated furnishes very interesting results, since the largest part is composed of hydrogen. A ton of English anthracite, for example, gives, at 1200° C., 318 cubic meters of gas composed of 291 cubic meters of hydrogen, or 91.4 per cent. There is no connection between the volume of gas liberated and the content of volatile matter in the fuel considered. Certain anthracites give volumes of gas just as great as the fatty oils, which contain larger quantities of volatile matter than the anthracites. The other constituents of the gas are carbon dioxide and carbon monoxide, with small quantities of metal. One might consider that the carbonization of the anthracite would constitute a source of hydrogen capable of being used in the manufacture of synthetic ammonia.

M. Maihle, continuing work on the production of petroleum by decomposition of vegetable oils, has shown that it is possible to use chloride of zinc as a catalyst in the hydrogenation. On heating different vegetable oils (peanuts, castor) or animal oils (requin, whale) with fused zinc chloride, the liberation of acrolein was accomplished and products boiling between 110° and 310° C., composed of a mixture of methane and ethylene hydrocarbons analogous to petroleum, were formed. Chloride of magnesium gives similar results.

Estimate of the Value of Fertilizer

I suggested in a previous letter that it would be interesting to estimate the increase of efficiency of plants under the action of various fertilizers, and I mentioned that the determination of sugars or of other principal constituents would give the most precise results.

M. Blaringhem, professor at the Conservatory of Arts and Measures, proposes using a method which is purely biologic and founded on genetic experiments. He took crops of barley, linen, and poppies. He subjected them to the action of various fertilizers: potash, nitrogen, phosphoric acid, limestone; then he weighed the test plants and the treated plants—for the barley, the proportion between the length of the third mark under the head and that of each corresponding—for the linen, he measured the thickness of the foliage, that is, the distance between each leaf on the same part of the stalk. He found, for example, that in the last case the foliage density, which was 11 to 12 for the test plants, equaled 16 for the linen subjected to potash fertilizer, and 24 for the linen subjected to nitrogen fertilizer.

. . . .

The Third Congress of the Society of Chemical Industry will meet in Paris, from the 20th to 25th of October. It will be particularly devoted to the agricultural applications of chemistry.

August 30, 1923

Personals *(Concluded)*

F. A. McMillin has resigned his position on the staff of the chemistry department of the University of Washington to take charge of the department of chemistry at the Idaho Technical Institute, Pocatello, Idaho.

A. A. Orlinger has resigned his position as chemical engineer and assistant chief chemist of the Henry Souther Engineering Co., Hartford, Conn., to become chemical engineer and chemist for the Warren Manufacturing Co., with headquarters at Milford, N. J.

V. F. Parry, formerly of the Pittsburgh station of the Bureau of Mines, is now a research chemist for the Combustion Utilities Corp., Long Island City, N. Y.

Arthur E. Rice, president of the Pennsylvania Salt Manufacturing Co., Philadelphia, Pa., died suddenly August 26 at the Canyon Hotel, Yellowstone Park, where he was spending a vacation. He was fifty-two years of age.

Elliott S. Robinson has been appointed assistant director of the Division of Biologic Laboratories of the Massachusetts State Department of Public Health.

E. S. Stateler has recently resigned his position as an Industrial Fellow at Mellon Institute to do research and developmental work for Hershey Brothers, manufacturers of chocolate, in Pittsburgh, Pa.

V. H. Wallingford, who recently returned from a year's study and travel as a fellow of the Commission for Relief in Belgium Educational Foundation, has accepted a position as research chemist with the Mallinckrodt Chemical Works, St. Louis, Mo.

W. C. Weltman, formerly chemist for the State of Illinois, is now first assistant chemist for the St. Louis, San Francisco Railroad Co., Springfield, Mo.

George Wilson, formerly instructor of chemistry at Purdue University, Lafayette, Ind., is now employed in the Research Bureau of the Aluminum Company of America.

N. E. Woldman has resigned his position as instructor of electrochemistry at the University of Maine, to accept an assistantship in the department of chemistry of the University of Illinois, where he will continue his studies for his doctor's degree. Mr. Woldman was formerly secretary-treasurer of the Maine Section of the American Chemical Society.

GERMAN LETTER

By Herr Hobein, Ebenhausen bei München, Bayern, Germany

Extended Patent Rights

A German law of 1920 specifies that rights of patents and copyrights which could not be worked during the war can be extended beyond their legal duration. Accordingly, the interval from August 1, 1914, to July 31, 1919, is not reckoned in the legal duration of a patent. At the same time the law grants to anyone who between the expiration and extension of a patent right has made use of the recently freed invention, the continued use without a license.

As to whether an unlicensed continuance should be allowed to one who had already worked the invention before the expiration of the patent right under infringement of the same and had continued in it afterward, there were different opinions. Through a decision of March 17, 1923, the court has now decided in favor of the inventor, in that it denies to the patent infringer the right of unlicensed continuance.

Hans Goldschmidt

Prof. Hans Goldschmidt, well known in scientific and technical circles, leader and promote of the Chemischen Fabrik Th. Goldschmidt A.-C. in Essen, died on May 31, at the age of sixty-two years. His most important accomplishment was the perfection of the Thermit process, which has found its greatest use in the welding of rails and tubes, and the mending of broken parts of machinery. It is based on the great heat of reaction which aluminium develops in burning to aluminium oxide, whereby the heavy metal oxides such as iron oxide lose oxygen, and are reduced to a molten metal. Through the aluminium-thermo process it was first possible to prepare chromium, manganese, molybdenum, and their compounds such as ferrochrome, ferrovanadium, etc., pure and free from carbon. The Franklin Institute has honored Dr Goldschmidt with the Elliot-Cresson Medal.

New Developments in the Lead Chamber Process

In spite of the introduction of the contact process for the production of sulfuric acid, the lead chamber process continues to hold its place. The repeated successful attempts to make it more profitable are directed toward limiting the large requirement of lead which the construction of the chambers requires and the large amount of necessary space, at the same time procuring conservation or increase of efficiency.

An excellent solution of the problem for the past fifteen years has been the approved Opl-tower system. It uses, instead of lead chambers, trickling towers, and in place of nitrous gases the quickly reacting liquid nitrous acid. The latter has been used also for several years in connection with the centrifugal-drum process of Schmiedel-Klencke. It is a characteristic of this process that the nitrous acid is brought by means of plunging, rapidly rotating drums into very intimate contact with the sulfur dioxide gases. In this way a very complete and quick absorption is accomplished. The process is especially valuable for the preparation of roasting gases with low and varying content of sulfur dioxide.

In a recent article in *Chemiker Zeitung*, Herr Opl, the inventor of the first-mentioned tower process, recommends taking a further step and constructing trickling towers of single iron tanks. This metal is not attacked by 50 to 60-degree acids. In six vessels of about 4 cubic meters volume, connected one behind the other, the formation of sulfuric acid is said to be effected in such a manner that the roasting gases under certain conditions may be converted into nitric acid. With such a system of six iron vessels Herr Opl obtains the same efficiency as with a normal-sized tower system taking ten times the amount of space.

Research on Chlorination Processes

Chlorine roasting consists, as is well known, in heating copper ores with the addition of alkali or alkali-earth chlorides in the presence of air, by which the copper is changed into a water and acid-soluble form consisting of a mixture of chloride, sulfate, and oxide. This process is especially adapted for manufacture from very poor ores or copper waste. Professor Tafel, in Breslau, has recently completed systematic research on this process and gave a report of it at the convention of German smelters and miners. His work is at present limited to the behavior of copper sulfide, the most important constituent of copper-containing iron pyrites waste, for whose preparation in Germany the chlorine roasting is used.

The results are important for the theory and practice of the process. It has been shown that it is not usually necessary to attain the previously prescribed temperature of 500° to 600° C. Moreover, one of 350° to 375° C. is considerably more favorable. The theoretically required quantity of chlorinating material is given in the proportion of 1 part copper, 1 part chlorine—for example, $Cu_2S : 2NaCl$. Potassium and calcium chlorides work more energetically than sodium chloride. In order that the addition of acid may not be needed air is admitted in small quantity. Steam is not necessary for bringing about the reaction, neither is the presence of iron.

Hints as to the Durability of Lead Containers

It often happens in chemical industries that lead containers are attacked by acids, while the same lead material will resist the same acids at equivalent temperatures in the laboratory. Herr Salvisberg points out in *Chemiker Zeitung* that galvanic currents may be the cause of this corrosion. The possibility of their origin through the contact of the two metals is suggested, as this is the case with lead-covered iron containers. In order to remedy this difficulty the apparatus should either be completely insulated so that no contact with the earth can take place, or, if this is not possible, the current strength and potential drop through the conductor should be determined by instruments, and an equal opposite current sent through the apparatus. The result is said to be surprising.

New Method of Titrating Silver and Halogen Ions

Concerning this subject Professor Fajans, of München, has written considerable, and recently has delivered a lecture before the convention of the German Bunsen Association for Practical Physical Chemistry. He has found that if to a very thin, green fluorescent solution of sodium fluorescein and alkali chloride, bromide, or iodide, is added gradually silver nitrate, in exceeding the equivalence point a sudden change to a red color occurs. On back-titrating with a very small excess of halogen ions the original color is recovered. Similarly, the halogen substitution products of the fluorescein can be used as indicators. The phenomenon is based on the fact that the colloidal silver halide portions adsorb the excess silver halide ions. To the silver ions of the silver halides and especially to the adsorbed excess silver ions can be added the dyestuff anions, and the red colors peculiar to the undissociated salts of these dyestuffs result. By adding excess halogen ions the dyestuff anions at the surface can be precipitated.

News of the Dye Industry

Professor Kalb, of München, announces that the shade of a dye, with other properties, can be frequently changed with profit. For example, from the usual reddish blue indigo is obtained pure blue and greenish blue chlorine and bromine derivatives. It is now possible, through high "iodination," to change the color of indigo still more, so that a pure green is obtained. The product obtained by the halogenation of indigo to green is of particular interest because only a very few green vat dyes are generally known. A simple process could be worked out for the production of high-iodinated indigoes.

New Processes of Microsublimation

A very simple device is described by Professor Kempf, of Berlin, in the *Zeitschrift für analytische Chemie.* The substance to be sublimed is heated in a very thin layer on an electric hot plate, the temperature of which is accurately regulated and can be kept constant within one degree. The sublimate is collected directly on the slides, which are placed immediately on the sublimation material. The apparatus can also be used in a vacuum and permits the microphotographical rendering of the sublimate.

August 6, 1923

BOOK REVIEWS

Atomic Structure and Spectral Lines. By ARNOLD SOMMERFELD. Translated from the third German edition by HENRY L. BROSE. xiii + 626 pages. E. P. Dutton & Co., New York, 1923. Price, $12.00.

The first German edition of this book was published in 1919, and contained 550 pages. The fact that this work has passed through two editions in a relatively short time is sufficient evidence of its popularity even in the original German form. The need of translating this monumental work into English has been felt for some time, and undoubtedly the present translation will be welcomed by a very large number of scientific men in England and America. The translator is to be complimented upon his work. Only on rare occasions does he slip into German idiom, but, on the whole, he has succeeded in producing an extremely readable work.

Nothing can indicate better the rapidity of progress in the particular realm of science which is the subject of the present work than the fact that almost three-quarters of it are devoted to a discussion of developments during the past decade. Bohr published his first paper in 1913, and in the same year Laue carried out his epoch-making investigation on the nature of X-rays. The various physical phenomena and theoretical speculations discussed by Sommerfeld may be regarded as originating largely in the discoveries of these two investigators.

The first two chapters are devoted to an excellent and yet concise discussion of such topics as the nature of cathode rays, canal rays, alpha and beta rays, the theory of X-rays based on classical electrodynamics, radioactive phenomena, nuclear charge, the periodic law, and theory of isotopes. The photo-electric effect is described and the author is thus able to introduce the experimental evidence obtained by Millikan and his collaborators for the validity of Einstein's law ($V\epsilon = h\nu$) and the existence of the quantum constant h. (This method of introducing the beginner to the quantum theory has always appealed to the reviewer as much simpler than the classical method which involves an abstract discussion of Planck's radiation laws.) Sommerfeld also points out that Bohr's fundamental equation $h\nu = W_e - W_a$ is the counterpart of Einstein's law.

The third chapter, X-ray Spectra, contains a discussion of the methods of measuring wave lengths and characteristic lines. In the fourth chapter the author shows that the quantum hypothesis may be expressed in the form of the postulate that the phase integral must be a whole multiple of the quantum of action h. Bohr's theory of the spectrum of hydrogen and ionized helium and the extension of this theory to include elliptic orbits are discussed very fully.

The fifth chapter contains a discussion of the most recent development in the quantum theory of spectral series, such as the principles of selection and correspondence, the application to Stark and Zeeman effect and the adiabatic hypothesis.

The quantum theory of series spectra in general is taken up very fully in Chapter VI, and shows how Bohr's theory has given us an interpretation of a vast amount of data so carefully compiled by spectroscopists and, by means of the relation of these to ionization and resonance potentials, has led to a deeper understanding of atomic structure. This marvelous success of a bold speculation will rank as one of the most epoch-making achievements in the history of science.

Chapter VII is devoted to the quantum theory of band spectra, and in Chapter VIII the author discusses his theory of the fine structure of spectral lines. The greatest interest attached to this theory is the fact that it furnishes experimental evidence for the Einstein theory of relativity.

While the author has not hesitated at the use of mathematical derivations in connection with the different topics, he has wisely kept out the more difficult mathematical treatment in each case and added this in the form of copious notes at the end of the volume.

While this work covers, to a certain extent, the same ground as that already covered so well by Foote and Mohler in their volume on "The Quantum Theory of Spectral Series," the reader will find in it an extremely valuable supplement to the latter.

SAUL DUSHMAN

The Manufacture of Acids and Alkalies. By GEORGE LUNGE, Ph.D. Completely revised and rewritten under the editorship of ALEXANDER CHARLES CUMMING, D.Sc.

Vol. I. Raw Materials for the Manufacture of Sulphuric Acid and Sulphur Dioxide. By WILFRID WYLD. xvi + 542 pages. Illustrated. D. Van Nostrand Co., New York, 1923. Price, $10.00.

Vol. V. The Manufacture of Hydrochloric Acid and Salt-Cake. By A. C. CUMMING. xvi + 424 pages. Illustrated. D. Van Nostrand Co., New York, 1923. Price, $8.50.

"Sulphuric Acid and Alkali," by George Lunge, has frequently been referred to as the "Bible of the heavy chemical industry." Originally published in 1879, it has from time to time been revised, extended, and brought into line with new developments in the manufacturing art.

The position of Dr. Lunge as a compiler of books on heavy chemical manufacture was somewhat different from other authors of similar works. Dr. Lunge had been a chemical manufacturer, and later professor and professor emeritus in the Federal Technical University, Zurich. He was an indefatigable reader and collector of data, and carried on an extensive correspondence with prominent men in the industry.

The place of "Lunge" in heavy chemical literature was therefore unique, and each new edition was a matter of considerable interest to chemical technologists because of the certain appearance of descriptions of new plants and processes.

After Dr. Lunge's death the question of his successor became a matter of great interest to the industry, and the appearance of the first volumes has therefore been awaited with some eagerness and curiosity.

The new editor, A. C. Cumming, has a difficult problem, and his method of attack is best illustrated by the following paragraphs from the Editor's Preface:

> It is doubtful if any one man could take up Dr. Lunge's task of describing adequately all the industries now dealt with in these volumes and it is certain that few would care to attempt it. Each volume will therefore be on a special subject and dealt with by a separate author who is responsible for that volume and is given a wide discretion in his treatment of the subject.
>
> The editor trusts that these united efforts will produce a new edition worthy of the great tradition which Dr. Lunge has established.

In effect, this apparently means the passing of "Lunge," as it has been known, and the appearance of a complete new work related only by title to the original.

Whether this new "Lunge" will some day occupy the position of Dr. Lunge's own work, cannot be decided on the first two volumes alone. The advertising pages at the end indicate that seven volumes are in preparation, with others to follow, so final judgment of the effort must await its completion.

Mr. Wyld's contribution to the series, "Raw Materials for the Manufacture of Sulphuric Acid and Sulphur Dioxide," follows the outline of Vol. I, Part 1, of the fourth (1913) edition of "Lunge." The historical preface and the properties of the raw materials are not greatly changed, but the rest of the matter has been brought up to date. Statistics were evidently compiled, as far as available, up to 1922, so they give a picture of the status and use of the raw materials of the sulfuric acid industry before, during, and after the World War.

There are some evidences of incomplete revision in the form of conflicting statements, as, for instance, on page 162: "Many years ago several works ran their nitre as a solution in water into the chambers. This has long since been discontinued* * * no independent favorable testimony has been published* * *," and on page 164, "According to the 50th Report of the Alkali Inspector, the application of a solution of nitrate of soda* * * to the first chamber has answered very well."

Interesting details of the supply of nitrogen oxides to chamber plants through oxidation of ammonia are given on pages 166 to 175. The statement on page 174 that this process had replaced "plotting" at all the works of the United Alkali Company (in England) should encourage trial installations on chamber plants in this country.

The chapter on pyrites burners is much more complete than the similar chapters in earlier "Lunges," doubtless because of Mr. Wyld's familiarity with mechanical furnaces.

Taken altogether, the new volume is a creditable piece of work, which displays throughout its 542 pages a painstaking effort to follow Dr. Lunge's practice and incorporate everything worth while.

Vol. V, "The Manufacture of Hydrochloric Acid and Saltcake," has been produced by the general editor, A. C. Cumming. It replaces Vol. II, Part 1, of "Lunge," but does not follow the same order of treatment of the subject. The last edition of Lunge, Vol. II, Part 1, was published in 1909, so there was a definite need for a revised edition incorporating the developments of the last fifteen years.

The first few pages of Dr. Cumming's volume bear evidence of a set task to be fulfilled as soon as possible. No other explanation would fit the inclusion of statistics on salt production and consumption exactly as in the 1909 "Lunge." Dr. Lunge gave his figures up to 1907. Dr. Cumming does not add any figures beyond 1907, and as the same wording appears, there is no suggestion of a desire to present current material, but rather the easy use of paste and shears.

In glancing through parallel pages of "Lunge" and Dr. Cumming's, the paste and shears become more evident. New material is so conspicuously absent that on arriving at page 188 a feeling of relief results from the sight of a drawing and descriptive matter of Six and Guttmann's mechanical saltcake furnace, not included in "Lunge."

The author had a chance to present new material on condensation equipment, direct manufacture from chlorine and hydrogen, and to give details on bulk movement of the acid in wood and rubber-lined metal, tank cars, but all these opportunities were passed over.

The theory of cooling and absorbing hydrochloric acid has received more attention in Dr. Cumming's volume, but even this phase has not been brought entirely up to date.

Mr. Wyld's volume is a contribution to the literature of the heavy chemical industry, but Dr. Cumming's "Hydrochloric Acid and Saltcake," in the reviewer's opinion, is not a worthy successor to Vol. II, Part 1, of "Lunge"—in fact, there does not appear to be much justification for its publication. It would seem to have been a more desirable policy to postpone the preparation of this particular volume until an author was found familiar with the subject and willing to take pains in collecting and presenting information.

A. E. Marshall

Forest Resources of the World. Vols. I and II. By Raphael Zon and W. N. Sparhawk. xiv + 997 pages. McGraw-Hill Book Co., Inc., New York, 1923. Price, $12.00.

We frequently see estimates of the amount of standing timber left in this country, the rate at which it is being cut and the rate at which new timber is growing. This publication is, however, the first in which complete information of this sort has been gathered together to cover the forest resources of all countries. The information given is not entirely statistical, but the character of the forests, the uses of the wood, and the general status of public and private forestry are discussed for each country. Typical headings for the arrangement of the information on the forests of each country are as follows: Forest Area, Character of Forest, Character of Ownership, Annual Cut, Annual Growth, Domestic Consumption, Exports and Imports, Wood-Using Industries, Forestry Education, Forest Laws, and Probable Future. In many cases the figures given are only estimates, but the amount of detailed information which has been gathered in regard to the forests of the world is surprisingly large.

The book is easy to read and the style is sufficiently varied to prevent it from becoming a monotonous repetition of statistical information. A series of new colored maps are provided, by which the character and location of the forests of different sections can be rapidly determined. These maps alone give more information on the general subject than has been gathered together into one previous publication.

The main part of the work of direct interest to chemists is the ninth chapter, Forest Resources Other than Timber. In this chapter the subjects of pulp and paper, resins, naval stores, rubber, tanning materials, dyewoods, cork, wood distillation, edible products, and vegetable oils are briefly discussed from the standpoint of statistics and supplies of raw material. This is not, however, the only place where these subjects are mentioned, since in every case where a country is important as a producer of chemical raw materials from the forests these materials are discussed under the heading of the wood-using industries of that country. To the chemist, therefore, the book will be of chief interest in giving complete and detailed information on the source of the chemical materials which come from the forest.

L. F. Hawley

Heat Transmission through Walls, Concretes, and Plasters. By Ezer Griffiths. 33 pages. H. M. Stationery Office, London, 1923. Price, 1s. 6d., net.

This pamphlet is a publication of the Building Research Board, Department of Scientific and Industrial Research of England, It gives a description of apparatus used and summary of results obtained in experiments conducted by the author to determine the rates of heat transmission through various types of wall construction common in English building practice.

The methods used in investigations are similar to those employed by American investigators. However, the materials reported on are not common to the building construction trade in this country. Therefore, a direct comparison with results obtained by investigators and authorities in this country is of little value.

Appendices are included in the book which describe wall constructions experimented on over an extended period by Norwegian investigators, also a summary of results obtained by a committee appointed by the Academy of Engineering Science, Stockholm, Sweden.

The conclusions laid down as the results of the Norwegian experiments, as well as the principles embodied in a new type of German wall construction briefly described, are interesting and well worth study by those interested in the conservation of heat used for industrial buildings, as well as dwelling houses.

Edgar C. Raek

A Symbol of Safety. By Harry Chase Brearley. xiv + 290 pages. Doubleday Page & Co., New York, 1923. Price, $2.50.

The "Symbol of Safety" is the label of the Underwriters' Laboratories, Inc., and Mr. Brearley's book is a review of the activities and significance of the work of this institution.

In a general way most of us are familiar with some form of equipment carrying the label "Underwriters' Laboratories Inspected," whether it be a fire extinguisher, a valve, a ladder, or even a Christmas tree lighting outfit. We also have a hazy idea (unless our work has brought us into direct contact with the laboratories) that the label means a standard of construction and performance.

The book, while essentially written for the nonscientific reader, gives a clear picture of the development and growth of Underwriters' Laboratories, from a single room and a total force of three in 1893 to a main testing plant occupying 55,000 square feet, two branch laboratories, and employing four hundred and fifty people in 1922.

The story is interesting to the chemist and the engineer, as it shows the gradual appreciation by outside interests of the reliability and value of laboratory testing methods.

The present scope of the testing work of Underwriters' Laboratories will surprise most readers of the book. Certificates of air-worthiness for aeroplanes, rating of automobiles as regards fire hazards, testing of gasoline supply systems, and determination of the ultimate breaking point of building columns under load and conflagration conditions, are some of the unexpected features of the laboratories' operations.

The important position of Underwriters' Laboratories in relation to industry is indicated by the statement that over half a billion labels were issued and applied to inspected equipment in 1922.

The book, despite its nontechnical language, is well and interestingly written. It is free from evident errors and bears internal evidence of careful revision.

The illustrations are remarkably good, and as they occupy 75 pages in comparison to 247 pages of text matter, it would seem that the photographer, following current motion picture practice, should have received title page acknowledgment.

A. E. Marshall

Material Handling Cyclopedia. Edited and compiled by Roy V. Wright, John G. Little, Robert C. Augur, and seven others. 847 pages. Simmons-Boardman Publishing Co., New York, 1921. Price, buckram $6.00; leather, $12.00.

As its name implies, this volume is a complete compendium of information on tools for handling materials. It consists of three distinct sections. The first section is a dictionary of the terms used later, and thus a reasonably complete dictionary of the terms in general use in this kind of work. Probably the most interesting point about this section is that it serves as the general index to the volume. After each definition is noted the page or pages in the later sections on which full discussion of that subject is to be found. This innovation might well be followed by other compilers of such compendia, for certainly it couples the idea directly with its full explanation. However, one unfamiliar with the scheme on which this index is built will search in vain through the book for the customary general index, as the only other one included is a table of contents listing the sections and chapters in the order in which they are treated. The dictionary itself is divided into two parts, one dealing with general terms and the other with electrical terms.

The second section is entirely descriptive of material handling equipment and makes up more than half of the whole book. Here qualified individuals discuss the various phases of the problems met under the following chapter headings: Hoisting Machinery, Package Handling Conveyors and Elevators, Loose Material Conveyors and Elevators, Conveying Machinery Details, Elevators, Trackless Transportation, Industrial Rail Transportation, and Handling Systems.

The third section is devoted to advertising. It is interesting to note the method of handling this material, which, incidentally, is well indexed and cross indexed. The pages are made up in strict conformity with the preceding text section and the only indication of their advertising nature is that the signature of the advertiser appears at the bottom of each page. No typographical displays of any kind are included, and as one glances through the book it is not at all obvious where one section ends and the other begins.

NEW BOOKS

Aluminium Facts and Figures (Vest Pocket Edition). 55 pp. Price, 2s. 6d. The British Aluminium Co., Ltd., London.

Chemical Resistance of Engineering Materials. Marston Lovell Hamlin and Francis Mills Turner, Jr. 264 pp. Price, $5.00. Chemical Catalog Co., Inc., New York.

Chemistry as a Career. A Synopsis of Lectures Given by the Registrar before College Chemical Societies during 1921–1923. Institute of Chemistry of Great Britain and Ireland, London.

Course in General Chemistry, Including an Introduction to Qualitative Analysis. William C. Bray and Wendell M. Latimer. 148 pp. Price, $1.60. The Macmillan Co., New York.

Cultivation of Lac in the Plains of India. Rai Bahadur C. S. Misra. Bulletin No. 142, Agricultural Research Institute, Pusa. 83 pp. Price, Rs. 1 8As. Superintendent of Government Printing, Calcutta.

Dictionnaires Techniques Illustrés en Six Langues. Francais-Allemand-Anglais-Russe-Italien-Espagnol. A. Schlomann. 13 volumes, each devoted to a separate branch of engineering and industry. Dunod, Paris.

Domain of Natural Science. E. W. Hobson. The Gifford Lectures Delivered in the University of Aberdeen in 1921 and 1922. 510 pp. Price, $6.50. The Macmillan Co., New York.

Fundamentals of Organic and Biological Chemistry. Thomas Guthrie Phillips. 260 pp. Price, $2.00. D. Appleton & Co., New York.

Hydraulics for Engineers and Engineering Students. F. C. Lea. 4th edition. 594 pp. Price, $6.00 net. Longmans, Green & Co., New York. A revised and enlarged edition, intended to be of value not only to practicing engineers but to students.

Laboratory Experiments in Chemistry to Accompany Black and Conant's "Practical Chemistry." H. Henry Black. 167 pp. Price, 80 cents. The Macmillan Co., New York.

Materie, Elektrizitat, Energie; Die Entwicklung der Atomistik in den Letzten Zehn Jahren. W. Gerlach. **Vol. VII. Wissenschaftliche Forschungsberichte. Naturwissenschaftliche Reihe,** edited by R. E. Liesegang. 195 pp. Price, 3s. 3d. T. Steinkopff, Dresden and Leipzig.

Mineral Industry of the British Empire and Foreign Countries. Statistics, 1919–21. Tin. Imperial Mineral Resources Bureau. 44 pp. Price, 1s. 6d. H. M. Stationery Office, London.

Neueren Chemotherapeutischen Präparate aus der Chininreihe (Optochin, im Besonderen Eukupin und Vuzin) und aus der Akridinreihe (Trypaflavin, Rivenol). E. Laqueur, assisted by A. Grevenstuk, A. Sluyters, and L. K. Wolff. 90 pp. Price, paper, 3s. Julius Springer, Berlin.

Organic Analysis, Qualitative and Quantitative. E. de Barry Barnett and P. C. L. Thorne. 180 pp. Illustrated. Price, $2.25. D. Van Nostrand Co., New York.

Preliminary Experiments in the Low-Temperature Carbonisation of Coal in Vertical Retorts. Fuel Research Board. *Technical Paper* **7.** Department of Scientific and Industrial Research. 27 pp. Price, 10d. H. M. Stationery Office, London.

Production of Liquid Fuels from Oil Shale and Coal in Australia. R. E. Thwaites. Institute of Science and Industry. *Bulletin* **24.** 62 pp. Government Printer, Melbourne.

Soils, Their Property and Management. T. Lyttleton Lyon, Elmer O. Fippin, and Harry O. Buckman. Rural Textbook Series. 764 pp. Illustrated. Price, $3.25. The Macmillan Co., New York.

Tabelle und Anleitung zur Ermittelung des Fettgehaltes nach Vereinfachtem Verfahren in Narhungsmitteln. Futtermitteln und Gebrauchsgegenstanden. J. Grossfeld. 12 pp. Price, 1s. J. Springer, Berlin.

Text Book of Physics for the Use of Students of Science and Engineering. Parts II and III. Heat and Light. J. Duncan and S. G. Starling. 314 pp. Price, $2.00. The Macmillan Co., New York.

Viscosity of Cellulose. R. D. Report No. 22 (Part III). Price, 1s. 9½d. H. M. Stationery Office, London.

GOVERNMENT PUBLICATIONS

Commerce Reports—August

Notice—*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, D. C. The regular subscription rate for these Commerce Reports mailed weekly is $3.00 per year (10 cents per single copy), payable in advance to the Superintendent of Documents, Government Printing Office, Washington, D. C.*

The Hide and Leather Division of the Department of Commerce has received a list of the **tanneries** in the Department of Valle del Causa, Colombia. This list is available to firms registered on the Exporters' Index. (P. 343)

The President of Mexico has signed a decree which exempts from import duties all **petroleum** imported into Mexico for the purpose of refining. This concession is made to assist the Mexican refining industry which has been passing through a severe crisis because of the scarcity of oil coming from the Mexican fields for refining. (P. 351)

The annual consumption of **paraffin wax** in Constantinople is between 1000 and 2000 sacks, of which 75 per cent is supplied by American firms and the remainder by Rumania. The prospects for the future development of the trade in paraffin in Turkey appear to be good. (P. 352)

There is a small but consistent demand for **calcium carbide** in the Colombo consular district, and at present the United States is not on the list of suppliers. (P. 360)

Honduras offers a rapidly expanding market for **paints.** (Pp. 360–1)

The annual report of the Harzgesellschaft shows that in the year 1922, 127 tons of **resin** were extracted. From this amount 88,000 kilos of finished resin and 20,500 kilos of turpentine were obtained. The Deutsche Harzgesellschaft has enlarged its works and has leased new ground and an increased production is anticipated. (P. 361)

The German press is now emphasizing the desirability of concluding an arrangement with Russia to open up the latter's enormous **phosphate** resources and convert the raw material to superphosphate on the ground in chemical plants operated by Germany. (Pp. 361–2)

According to certain German dealers, wages and salaries in Baden have increased to such an extent that certain **chemicals** can be imported at a lower price than it would cost to manufacture them in Germany. Stuttgart dealers claim that prices of chemicals in the occupied areas are approximately 50 per cent lower than in the unoccupied areas. (P. 362)

The use of **calcium carbide** is gradually decreasing in the state of Sao Paulo, Brazil. (P. 362)

Intensified activity on the part of **oil shale mines** owned by the Esthonian government resulted in a considerable increase in the total value of the production in 1922 as compared with previous years. (P. 417)

The exports of **chemicals** and **allied products** from the United States for the first six months of 1923 had an aggregate value of $75,125,022, an increase of 21 per cent over the first six months of 1922 and equivalent to 67 per cent of the total value of $112,836,432 for the entire year 1922, June being the record month. (Pp. 419–22)

An American concern is to build a **kraft pulp mill** in Ontario, Canada, with a minimum daily capacity of 75 tons. The manufacture of kraft paper is a new development in that community and will bring into use a wider variety of woods than has been used. (P. 431)

The importation into Mexico of all **narcotic drugs,** except by the Public Health Department of the government, has been prohibited. (P. 438)

Figures are given showing the new increase in Polish consumption taxes on **mineral oils.** (P. 440)

A new **Swiss carburetor** has been invented with features that permit the use of benzene, gasoline, kerosene, or alcohol, without alteration of the carburetor. (P. 463)

The Japanese **heavy chemicals** and **dyestuffs** market in 1922 is reviewed. It is pointed out that the United States has not held the position which it gained during the war, with the single exception of the trade in sulfate of ammonia. For other heavy chemicals and dyestuffs Japan is now turning to England and Germany, principally because better prices can be had from those countries. (Pp. 465–6)

Statistics are given showing the Canadian production, imports, and exports of **arsenic** in 1921 and 1922. (P. 466)

Interested parties may obtain from the Bureau of Foreign and Domestic Commerce a complete list of the names and addresses of **quinine plantations** in the Netherlands East Indies. (P. 466)

The Chilean Congress is considering the question of having an **international exposition** of products relating to **mining, metallurgy,** and **nitrate** at Santiago in 1924. (Pp. 479–80)

A general feeling of optimism characterizes the **petroleum** situation in Rumania. Production is good and on the whole there is considerable confidence in the situation. (P. 481)

Small quantities of **Cuban motor alcohol** have been imported recently into the Canary Islands for experimental purposes with a view to the introduction of that product there. (P. 483)

The construction of the canal through the Coyuca and San Jeronimo lagoons in Mexico is bringing to light an almost inexhaustible supply of **mangrove,** the bark of which is used so extensively in the tanning industry. (P. 487)

It is estimated that the **Swedish wood pulp** production for this year, instead of being normal (approximately 880,000 metric tons), will be about 720,000 metric tons, of which about 535,000 tons will be available for export. Production has been lowered because of labor troubles. (P. 488)

By a recent Mexican decree all products obtained from foreign **petroleum** imported for refining will pay only 15 per cent of the current quotas and will be exempt from the Mexican export duties. (P. 497)

The **Scottish mineral oil industry** has survived the stress of recent years and is now in practically full operation. (P. 537)

Both the import and export trade of the United States in **chemicals and allied products** have been on the upswing during the first six months of 1923. An exact comparison of the import trade with corresponding months of 1922 cannot be made owing to the change in classification necessitated by the alterations in the import schedule. A conservative estimate, however, would place the gain in incoming shipments at over 40 per cent. (Pp. 543–4)

Samples of a **wood fiber,** known in the state of Vera Cruz as "jonote," have been received in the Textile Division of the Bureau of Foreign and Domestic Commerce, and are available for inspection. (P. 551)

In accordance with the Commercial Treaty between Austria and Italy, the latter has agreed to grant **special rates** on the following commodities imported from Austria: articles of copper, nickel, zinc, and their alloys; magnesite bricks; carbonic acid, copper sulfate, ammonium sulfate; varnishes; glue; and pulp for the manufacture of paper. Austria, on the other hand, has agreed to admit the following Italian goods at special rates: olive oil; essential oils; sulfur; boric, tartaric, and citric acids; borax; ammonium sulfate, calcium citrate, copper sulfate; superphosphates; calcium cyanide; and oilseed cakes. (P. 562)

Italy has **modified** her general customs **tariff rates** on the following American products: artificial silk; aluminium and its alloys; essence of turpentine; sodium carbonate; barium chloride; lithopone; chemical fertilizers, including calcium cyanamide and impure nitrate of ammonium; formaldehyde; and organic synthetic colors. (P. 563)

Italy has slightly reduced her customs tariff on American **ferro-alloys.** (P. 564)

Latvia has placed an import duty on **salt.** (P. 564)

All materials and machinery for use in the manufacture of **ether alcohol** within the Republic of Salvador may be imported free of duty. (P. 565)

Statistics of Exports to the United States

Germany—(P. 466)
  Heavy chemicals
  Dyes and dyestuffs

Canada—(P. 488)
  Wood pulp

Tampico, Mexico—(P. 483)
  Petroleum
  Gasoline

Special Supplements Issued

Algeria
Danzig
Finland
Indo-China
Uruguay
Venezuela

Austrian Trade in Rubber Products. C. H. Foster. *Trade Information Bulletin* **131.**

Polish Petroleum Industry in 1922. *Trade Information Bulletin* **135.**

The Brazilian Market for Paper and Paper Products. *Trade Information Bulletin* **127.**

Notice—*Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate.*

Bureau of the Census

Chemicals and Allied Products. 14th Census of the United States, Manufactures, 1919. Prepared under the supervision of E. F. Hartley. 187 pp. 1923.

Essential Oils. Manufactures, 1921. 8 pp. Paper, 5 cents.

Explosives. Manufactures, 1921. 10 pp. Paper, 5 cents.

Pulp-Wood Consumption and Wood-Pulp Production. Compiled in coöperation with the Department of Agriculture, Forest Service. Forest Products, 1921. 13 pp. Paper, 5 cents.

Turpentine and Rosin. Manufactures, 1921. Compiled in coöperation with the Department of Agriculture, Bureau of Chemistry. 10 pp. Paper, 5 cents.

Bureau of Mines

Accidents at Metallurgical Works in the United States during the Calendar Year 1921. W. W. Adams. *Technical Paper* **327.** 31 pp. Paper, 5 cents.

Carbon Tetrachloride Extinguisher on Electric Fires. S. H. Katz, E. J. Gleim, and J. J. Bloomfield. *Reports of Investigations* **2499.** 16 pp. Issued July, 1923.

Coal-Mine Fatalities in June, 1923. W. W. Adams. *Reports of Investigations* **2508.** 4 pp. Issued July, 1923.

Comparative Tests of By-Product Coke and Other Fuels for House-Heating Boilers. Henry Kreisinger, John Blizard, H. W. Jarrett, and J. J. McKitterick. *Technical Paper* **315.** 21 pp. Paper, 5 cents.

Disastrous Inflammation of Coal Dust in Excavating a Mine Dump. C. A. Herbert. *Report of Investigations* **2498.** 2 pp. Issued July, 1923.

Experiments on Fan-Pipe Installations at Butte, Montana. G. E. McElroy and A. S. Richardson. *Reports of Investigations* **2509.** 14 pp. Issued July, 1923.

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The Alkali Problem in Irrigation. C. S. Scofield. From the Smithsonian Report for 1921. *Publication* **2681.** 11 pp.

MARKET REPORT—SEPTEMBER, 1923

[SUPPLIED BY DRUG & CHEMICAL MARKETS]

Now that the summer is over and the trade looks back on the total volume of business actually consummated, the figures are not nearly as disappointing as the pessimistic reports heard during July and August would have led one to believe. Taken all in all, the volume of business during the summer was not below normal when compared with other years. Of course, in numerous instances prices were too low for a healthy market—that is, where they were below cost of production as a result of seasonal competition. As expected, the middle of September saw some expansion in demands. Buyers, however, do not appear anxious to abandon a policy of caution, with a consequence that the quantity of goods sold on each individual order is usually small, although orders are more frequently repeated.

One of the features of the market late in the month was an announcement of alkali prices for next year by a leading manufacturer. The prices for contracts are the same as those which have been maintained this year and last year. The prices are considered low when the increase in costs of production are taken into account, but the increase in volume of business during the past year to some extent offset the increased costs of production. The steady prices of alkalies have had a stabilizing influence on the chemical market as a whole. Heavy acids have been somewhat routine with the exception of sulfuric acid which has been moving steadily. Lactic acid has been in fair demand. Oxalic acid continues easy owing to lack of demand and competition. All cheap lots of ammonium chloride have been taken up and prices have advanced. Ammonium sulfate has been quiet but demand is expected to open up soon. Export demand for arsenic has kept this item moving better than it otherwise would be, since domestic demand has fallen off after the disappointing season for calcium arsenate this summer. Arsenic has climbed back to 11 cents per pound mainly through the call from European countries. Calcium arsenate is nominal as sellers endeavor to liquidate stocks left over from the past season.

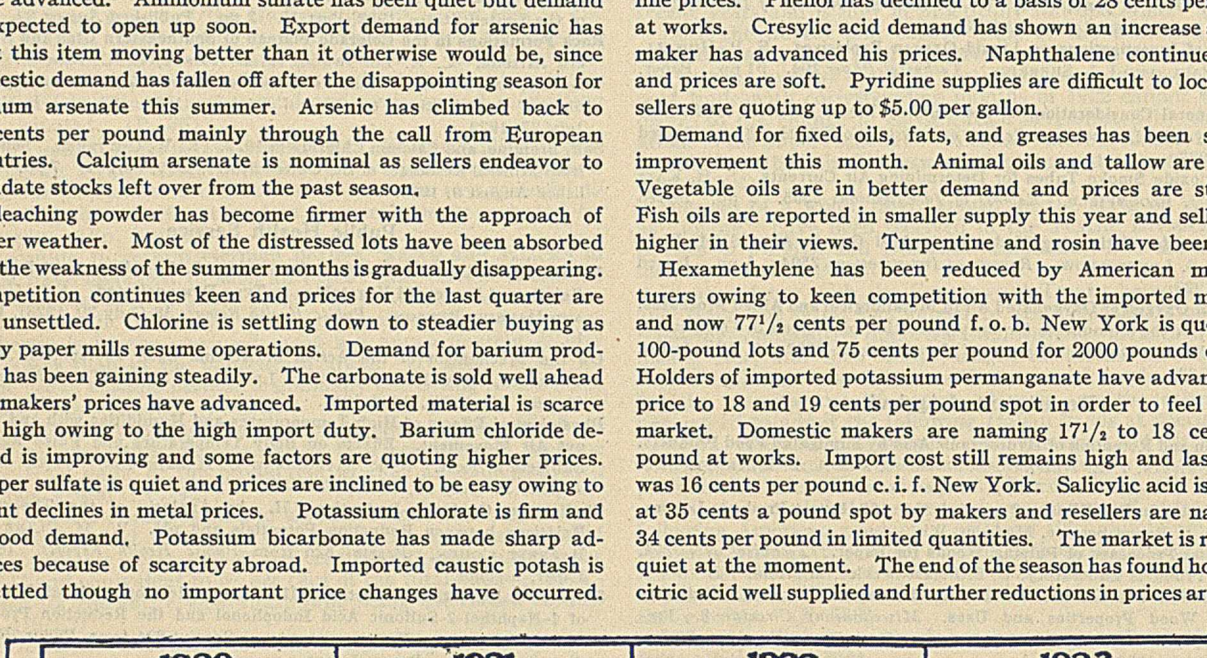
Bleaching powder has become firmer with the approach of cooler weather. Most of the distressed lots have been absorbed and the weakness of the summer months is gradually disappearing. Competition continues keen and prices for the last quarter are still unsettled. Chlorine is settling down to steadier buying as many paper mills resume operations. Demand for barium products has been gaining steadily. The carbonate is sold well ahead and makers' prices have advanced. Imported material is scarce and high owing to the high import duty. Barium chloride demand is improving and some factors are quoting higher prices. Copper sulfate is quiet and prices are inclined to be easy owing to recent declines in metal prices. Potassium chlorate is firm and in good demand. Potassium bicarbonate has made sharp advances because of scarcity abroad. Imported caustic potash is unsettled though no important price changes have occurred. Recent changes in selling for export in Germany have kept the situation unsettled. Potassium prussiates continue quiet and prices are easier. Potassium bichromate has declined owing to slow demand and keen competition. Potassium permanganate is firm with a lone domestic maker competing with imported material.

Sodium compounds have undergone little change in prices or demand. Soda ash and caustic soda are in steady demand. Makers of sodium bichromate are quoting lower prices. Sodium prussiate declined during the month and then recovered again to its former position at 14 cents per pound. Sodium chlorate is firm. Sodium sulfide supplies are plentiful and prices are easy in the face of slow demand. Demand for Glauber's salt has not been active and supplies are not so small as usual for summer months. Tin crystals are higher for September owing to rising metal prices.

Demand for intermediates has begun to show improvement after the quiet period during the summer. Inquiries have become more frequent and orders for small amounts are coming in. Prices have shown little change except in the case of *o*- and *p*-toluidine. Both these products have advanced as demand continued to increase. β-Naphthol has been subject to some competition and sales have been reported below current quotations. Resale lots of intermediates have been few and scattered, and makers have the situation well in hand. Coal-tar crudes have become easier as supplies became more plentiful. Benzene has weakened considerably owing to the recent reductions in gasoline prices. Phenol has declined to a basis of 28 cents per pound at works. Cresylic acid demand has shown an increase and one maker has advanced his prices. Naphthalene continues quiet and prices are soft. Pyridine supplies are difficult to locate and sellers are quoting up to $5.00 per gallon.

Demand for fixed oils, fats, and greases has been showing improvement this month. Animal oils and tallow are higher. Vegetable oils are in better demand and prices are stronger. Fish oils are reported in smaller supply this year and sellers are higher in their views. Turpentine and rosin have been quiet.

Hexamethylene has been reduced by American manufacturers owing to keen competition with the imported material, and now $77^{1}/_{2}$ cents per pound f. o. b. New York is quoted for 100-pound lots and 75 cents per pound for 2000 pounds or over. Holders of imported potassium permanganate have advanced the price to 18 and 19 cents per pound spot in order to feel out the market. Domestic makers are naming $17^{1}/_{2}$ to 18 cents per pound at works. Import cost still remains high and last heard was 16 cents per pound c. i. f. New York. Salicylic acid is quoted at 35 cents a pound spot by makers and resellers are named at 34 cents per pound in limited quantities. The market is reported quiet at the moment. The end of the season has found holders of citric acid well supplied and further reductions in prices are likely.



Courtesy of Drug & Chemical Markets

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

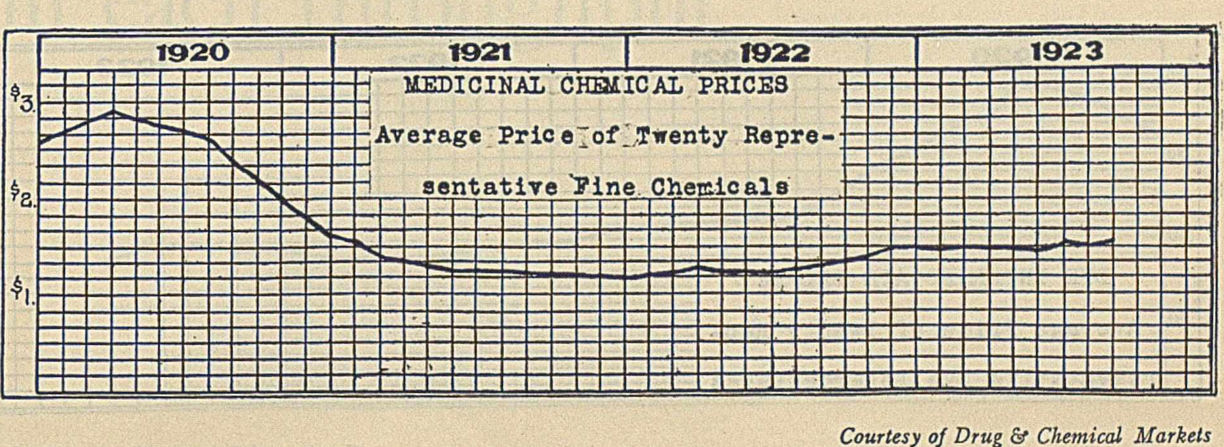
INORGANIC CHEMICALS

	Sept. 1	Sept. 15	Jan. 1923
Acid, Boric, cryst. bbls.......lb.	.11	.11	.11½
Hydrochloric, comm'l. 20° lb.	.01¼	.01¼	.01¼
Hydrofluoric, 30% bbls...lb.	.07	.07	.06
Hydriodic, 10% U. S. P...lb.	.65	.65	.65
Nitric, 42°, cbys. c/1 wks. lb.	.05¾	.05¾	.06
Phosphoric, 50% tech....lb.	.08	.08	.08
Sulfuric, C. P...........lb.	.09	.09	.07
66° tks. wks.......ton	15.00	15.00	15.00
Oleum, 20%.......ton	19.00	19.00	18.00
Alum, Ammonia, lump.......lb.	.03½	.03½	.03½
Potash, lump...........lb.	*.03¼	*.03¼	*.03½
Chrome............lb.	.05½	.05½	.05½
Soda, ground...........lb.	.04	.04	.04
Aluminum Sulfate (iron-free).lb.	.02½	.02½	.02½
Ammonium Carbonate, pwd..lb.	.09	.09	.09½
Chloride, white gran.....lb.	.07½	.07½	.07½
Ammonia, anhydrous........lb.	.30	.30	.30
Ammonia Water, drums, 26°.lb.	.07½	.07½	.07½
Arsenic, white..............lb.	.10½	.11	.15½
Barium Choride............ton	*80.00	*82.50	*92.50
Nitrate................lb.	*.07¾	*.07¾	*.07½
Barytes, white.............ton	33.50	33.50	33.50
Bleaching Powd., 35%, works .... 100 lbs.	1.75	1.75	2.15
Borax, cryst., bbls..........lb.	.05½	.05¼	.05½
Bromine, pure,-wks..........lb.	.29	.29	.29
Calcium Chloride, fused, f.o.b. N. Y..................ton	24.50	24.50	24.50
Chlorine, liquid.............lb.	.05	.05	.05¼
Copper Sulfate......... 100 lbs.	5.10	5.10	6.25
Iodine, resublimed...........lb.	4.55	4.55	4.50
Lead Acetate, white crystals..lb.	.14	.14	.13
Nitrate................lb.	.22	.22	.22
Red.............. 100 lbs.	11.40	11.40	10.60
White (Carb.)..........lb.	.09¾	.09¾	.08½
Lime, live and hydrated, bbl..lb.	.01½	.01½	.01½
Oyster shell............lb.	.03	.03	.03
Lime Acetate.......... 100 lbs.	4.00	4.00	3.50
Magnesium Carbonate, tech..lb.	.08	.08	.08
Magnesite, calcined.........ton	55.00	55.00	55.00
Phosphorus, yellow..........lb.	*.35	*.35	*.28
Red...................lb.	—	—	*.30
Plaster of Paris, tech ....bbl.	3.30	3.30	3.30
Potassium Bichromate.......lb.	.10	.09¾	.10
Bromide, imported......lb.	.16	*.16	.14½
Carbonate, calc., 80–85%.lb.	*.06½	*.06½	*.05½
Chlorate, cryst..........lb.	*.07½	*.07½	*.05½
Hydroxide, 88–92%.....lb.	*.07¼	*.07¼	*.08
Iodide, bulk, U. S. P.....lb.	3.75	3.75	3.60
Nitrate................lb.	.06½	.06½	.06½
Permanganate, U. S. P...lb.	*.18	*.17½	*.16
Prussiate, red...........lb.	*.60	*.60	*.90
Yellow.............lb.	*.32	*.32	*.38
Salt Cake, bulk.............ton	24.00	24.00	28.00
Silver Nitrate...............oz.	.44	.44	.44
Soda Ash, 58%, bags....100 lbs.	*2.00	*2.00	*2.00
Caustic, 76%, N. Y. 100 lbs.	3.70	3.70	3.50
Sodium Acetate.............lb.	.05	.05	.07¼
Bicarbonate....... 100 lbs.	2.25	2.25	2.00
Bichromate.............lb.	.08	.08	.07¾
Bisulfite, powd..........lb.	.04	.04	.04
Chlorate................lb.	.06½	.06½	.06½
Cyanide, 96–98%.......lb.	.23	.23	.23
Fluoride, tech...........lb.	.09½	.09½	.09½
Hyposulfite, bbls... 100 lbs.	2.90	2.90	3.60
Nitrate, 95%...... 100 lbs.	2.42½	2.45	2.57½
Nitrite.................lb.	.07¼	.07¼	.08½
Prussiate, yellow........lb.	.14	.14	.18½
Phosphate (di-sod.), tech.lb.	.03½	.03½	.03½
Silicate, 40° ....100 lbs.	.80	.80	.80
Sulfide, 60%, fused......lb.	.04½	.04½	.05
Strontium Nitrate...........lb.	*.10	*.10	*.08¾
Sulfur, flowers.........100 lbs.	3.00	3.00	3.00
Crude, mines......long ton	14.00	14.00	14.00
Tin Bichloride, 50% sol'n....lb.	.12½	.12½	.10¼
Oxide..................lb.	.45	.45	.43
Zinc Chloride, U. S. P........lb.	.25	.25	.20
Oxide, bbls.............lb.	.08½	.08½	.07½

ORGANIC CHEMICALS

	Sept. 1	Sept. 15	Jan. 1923
Acetanilide, U. S. P., bbls....lb.	.35	.32	.35
Acid, Acetic, 28 p. c.... 100 lbs.	3.38	3.38	3.17½
Glacial ....100 lbs.	12.78	12.78	12.05
Benzoic, U. S. P.........lb.	.72	.72	.72
Carbolic, cryst., U. S. P., drums.............lb.	.30	.30	.32
50- to 110-lb. tins...lb.	.32	.32	.34
Citric, crystals, kegs.....lb.	*.50	*.50	*.48½
Oxalic, cryst., bbls., wks.lb.	.12	.12	.13½
Pyrogallic, resublimed...lb.	1.55	1.55	1.55
Salicylic, U. S. P.........lb.	.35	.35	.45
Tannic, U. S. P., bbls....lb.	.83	.83	.70
Tartaric, cryst., U. S. P...lb.	*.34	*.34	*.32
Acetone, drums.............lb.	.25	.25	.21
Alcohol, denatured, complete. gal.	.46	.46	.45
Ethyl, 190 proof, bbls...gal.	4.75	4.75	4.70
Amyl Acetate.............. gal.	4.50	4.50	2.50
Camphor, Jap, refined, cases .lb.	.93	.93	.86
Carbon Bisulfide, c/1........lb.	.06¾	.06¾	.06¾
Tetrachloride...........lb.	.10½	.10½	.10½
Chloroform, U. S. P., drums..lb.	.35	.35	.35
Creosote, U. S. P............lb.	.50	.50	.40
Cresol, U. S. P..............lb.	.36	.36	.25
Dextrin, corn ....100 lbs.	3.65	3.65	3.09
Imported Potato........lb.	.07	.07	.09
Ether, U. S. P., 100 lbs.......lb.	.13	.13	.13
Formaldehyde, bbls..........lb.	.13	.13	.16
Glycerol, dynamite, drums...lb.	.16	.16	.16½
Methanol, pure, drums......gal.	1.10	1.10	1.35
Methylene Blue, med........lb.	2.25	2.25	2.25
Petrolatum, light amber......lb.	.04½	.04½	.03¾
Pyridine ....gal.	4.00	4.25	2.75
Starch, corn, pow'd.....100 lbs.	3.22	3.22	2.47
Potato, Jap.............lb.	.05	.05	.06¾
Sago....................lb.	.04½	.04½	.03½

* Resale or Imported (not an American maker's price).



Courtesy of Drug & Chemical Markets

OILS, WAXES, ETC.

	Sept. 1	Sept. 15	Jan. 1923
Beeswax, pure, white..........lb.	.37	.37	.36
Castor Oil, No. 3.............lb.	.13½	.13	.13
Ceresin, yellow...............lb.	.08	.08	.08½
Corn Oil, crude, tanks, mills...lb.	.09	.10	.09¾
Cottonseed Oil, crude, f. o. b. mill.....................lb.	.10	.10	.09⅝
Linseed Oil, raw, lc/l........gal.	.90	.90	.87
Menhaden Oil, crude, mills...gal.	.40	.42½	.53
Neat's-foot Oil, 20°..........lb.	.15	.16½	.18½
Paraffin, 128–130 m. p., ref....lb.	.04	.04	.04
Rosin, "F" grade, 280 lbs....bbl.	5.90	5.95	6.25
Rosin Oil, first run..........gal.	.45	.45	.45
Shellac, T. N.................lb.	.57	.57	.80
Sperm Oil, bleached winter, 38°......................gal.	.99	.99	1.03
Stearic Acid, double pressed...lb.	.13½	.13½	.12½
Tallow Oil, acidless..........lb.	.09	.10½	.11½
Turpentine, spirits of........gal.	.95	1.02	1.56

METALS

	Sept. 1	Sept. 15	Jan. 1923
Aluminium, No. 1, ingots.....lb.	.25	.25	.23
Antimony, ordinary......100 lbs.	6.75	6.75	6.75
Bismuth.......................lb.	2.75	2.75	2.75
Copper, electrolytic..........lb.	.13⅝	.13⅞	.14¾
Lake.........................lb.	.13⅝	.13⅞	.14¾
Lead, N. Y..............100 lbs.	6.75	6.75	7.80
Nickel, electrolytic..........lb.	.29	.29	.36
Platinum, refined, soft........oz.	116.00	116.00	118.00
Quicksilver, flask......75 lbs. ea.	62.00	62.00	73.00
Silver, foreign...............oz.	.62⅝	.62⅝	.63
Tin...........................lb.	.40½	.42	.39
Tungsten Wolframite....per unit	8.50	8.50	7.50
Zinc, N. Y..............100 lbs.	6.75	6.85	8.25

FERTILIZER MATERIALS

	Sept. 1	Sept. 15	Jan. 1923
Ammonium Sulfate, expt. 100 lbs.	3.45	3.45	3.90
Blood, dried, f. o. b. N. Y...unit	3.75	3.75	4.70
Bone, 3 and 50, ground, raw..ton	25.00	25.00	28.00
Calcium Cyanamide, unit of ammonia...................	2.25	2.25	2.25
Fish Scrap, dried, wks.......unit	3.80	3.80	5.35 & .10
Phosphate Rock, f. o. b. mine:			
Florida Pebble, 68%.....ton	3.25	3.25	3.00
Florida, 70%...........ton	3.55	3.55	3.55
Florida, 74–75%........ton	4.50	4.50	4.50
Tennessee, 72%.........ton	5.50	5.50	5.25
Potassium Muriate, 80%....unit	.68	.68	.68
Tankage, high-grade, f. o. b. Chicago................unit	3.60 & .10	3.60 & .10	4.75 & .10

COAL-TAR CHEMICALS

Crudes

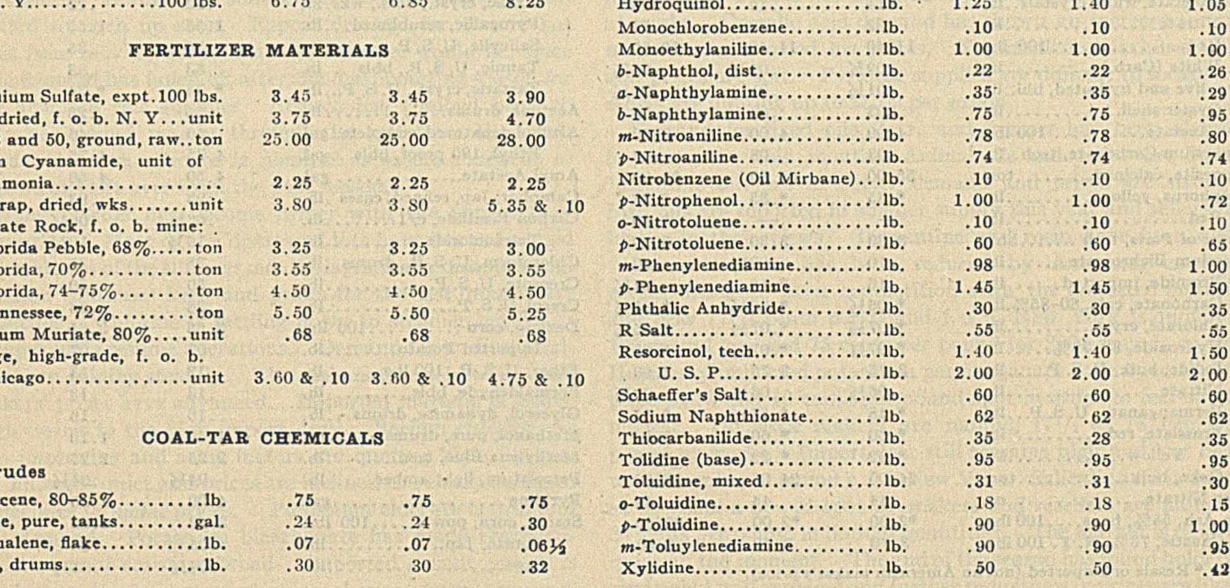
	Sept. 1	Sept. 15	Jan. 1923
Anthracene, 80–85%.........lb.	.75	.75	.75
Benzene, pure, tanks........gal.	.24	.24	.30
Naphthalene, flake...........lb.	.07	.07	.06½
Phenol, drums................lb.	.30	30	.32

Crudes (*concluded*)

	Sept. 1	Sept. 15	Jan. 1923
Toluene, pure, tanks.........gal.	.28	.28	.30
Xylene, 2 deg. dist. range, drums..................gal.	.65	.65	—

Intermediates

	Sept. 1	Sept. 15	Jan. 1923
Acids:			
Anthranilic..............lb.	.96	.96	1.10
Benzoic, tech............lb.	.70	.70	.65
Cleve's..................lb.	1.00	1.00	1.25
Gamma....................lb.	1.70	1.70	1.85
H........................lb.	.75	.75	.80
Metanilic................lb.	.60	.60	.60
Monosulfonic F...........lb.	2.30	2.30	2.30
Naphthionic, crude.......lb.	.62	.62	.60
Nevile & Winther's.......lb.	1.10	1.10	1.15
Picric...................lb.	.25	.25	.20
Sulfanilic...............lb.	.20	.20	.19
Tobias'..................lb.	1.30	1.30	1.30
Aminoazobenzene............lb.	1.15	1.15	1.15
Aniline Oil................lb.	.16½	.16½	.17
Aniline Salt...............lb.	.24	.24	.25
Anthraquinone (sublimed).....lb.	1.30	1.30	1.30
Benzaldehyde, tech...........lb.	.75	.75	.65
U. S. P..................lb.	1.50	1.50	1.40
Benzidine Base.............lb.	.82	.82	.84
Benzidine Sulfate..........lb.	.70	.70	.70
Diaminophenol..............lb.	3.80	3.80	3.75
Dianisidine................lb.	4.60	4.60	4.50
p-Dichlorobenzene..........lb.	.17	.17	.17
Diethylaniline.............lb.	.60	.60	.60
Dimethylaniline............lb.	.41	.41	.41
Dinitrobenzene.............lb.	.19	.19	.19
Dinitrotoluene.............lb.	.19	.19	.20
Diphenylamine..............lb.	.48	.48	.50
G Salt.....................lb.	.55	.55	.60
Hydroquinol................lb.	1.25	1.40	1.05
Monochlorobenzene..........lb.	.10	.10	.10
Monoethylaniline...........lb.	1.00	1.00	1.00
b-Naphthol, dist...........lb.	.22	.22	.26
a-Naphthylamine............lb.	.35	.35	.29
b-Naphthylamine............lb.	.75	.75	.95
m-Nitroaniline.............lb.	.78	.78	.80
p-Nitroaniline.............lb.	.74	.74	.74
Nitrobenzene (Oil Mirbane)...lb.	.10	.10	.10
p-Nitrophenol..............lb.	1.00	1.00	.72
o-Nitrotoluene.............lb.	.10	.10	.10
p-Nitrotoluene.............lb.	.60	.60	.65
m-Phenylenediamine.........lb.	.98	.98	1.00
p-Phenylenediamine.........lb.	1.45	1.45	1.50
Phthalic Anhydride.........lb.	.30	.30	.35
R Salt.....................lb.	.55	.55	.55
Resorcinol, tech...........lb.	1.40	1.40	1.50
U. S. P..................lb.	2.00	2.00	2.00
Schaeffer's Salt...........lb.	.60	.60	.60
Sodium Naphthionate........lb.	.62	.62	.62
Thiocarbanilide............lb.	.35	.28	.35
Tolidine (base)............lb.	.95	.95	.95
Toluidine, mixed...........lb.	.31	.31	.30
o-Toluidine................lb.	.18	.18	.15
p-Toluidine................lb.	.90	.90	1.00
m-Toluylenediamine.........lb.	.90	.90	.95
Xylidine...................lb.	.50	.50	.42



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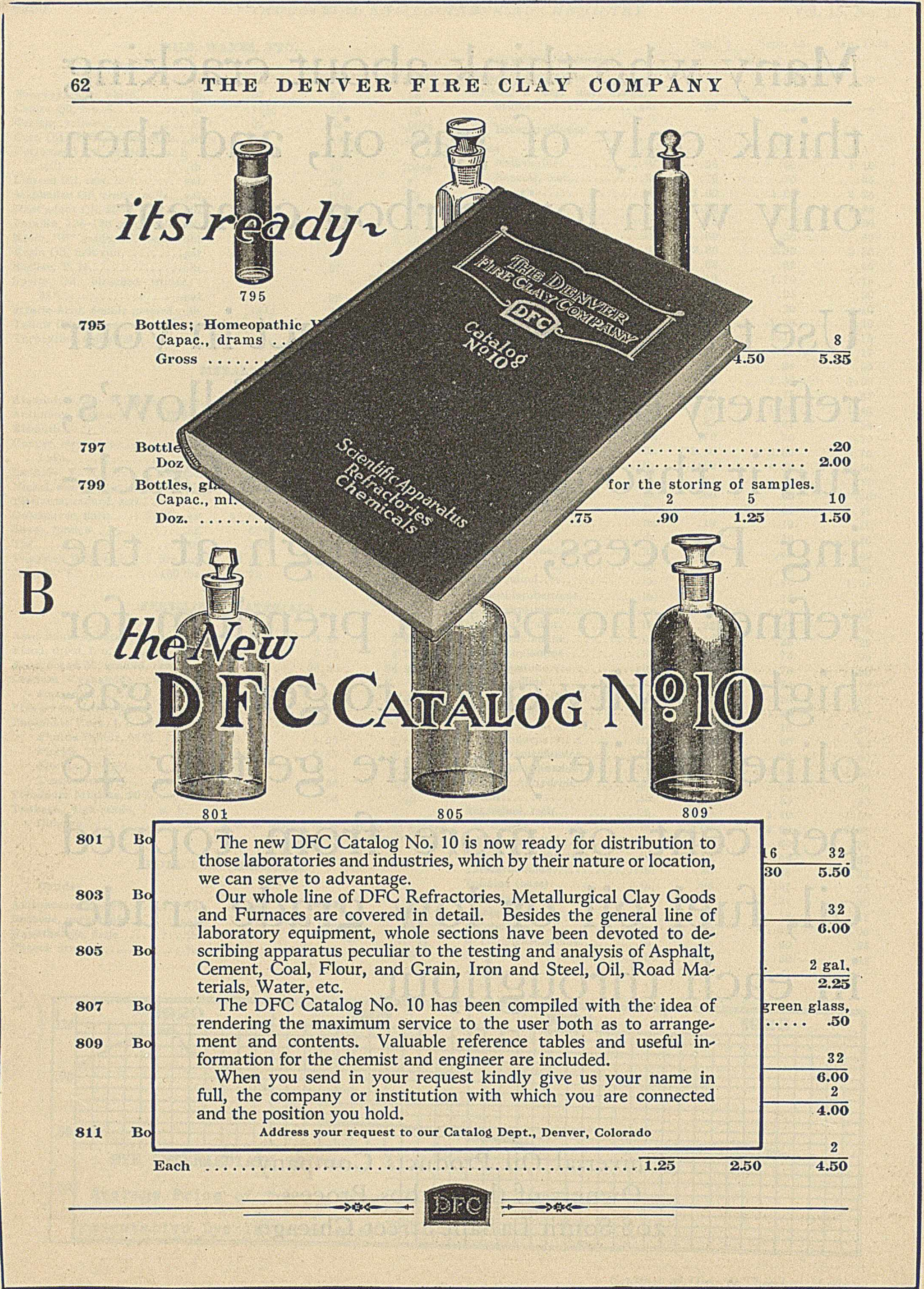
Average Price of Twenty Representative Dye Intermediates

Courtesy of Drug & Chemical Markets



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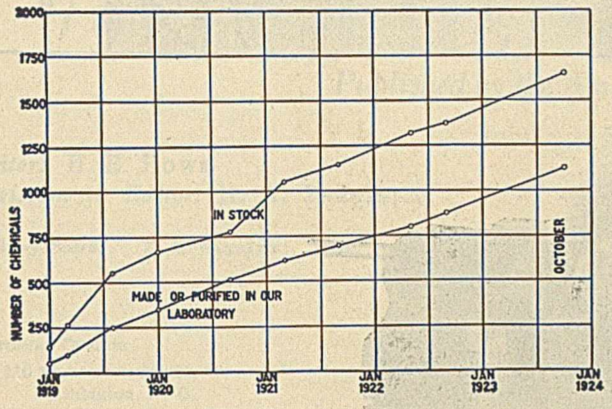

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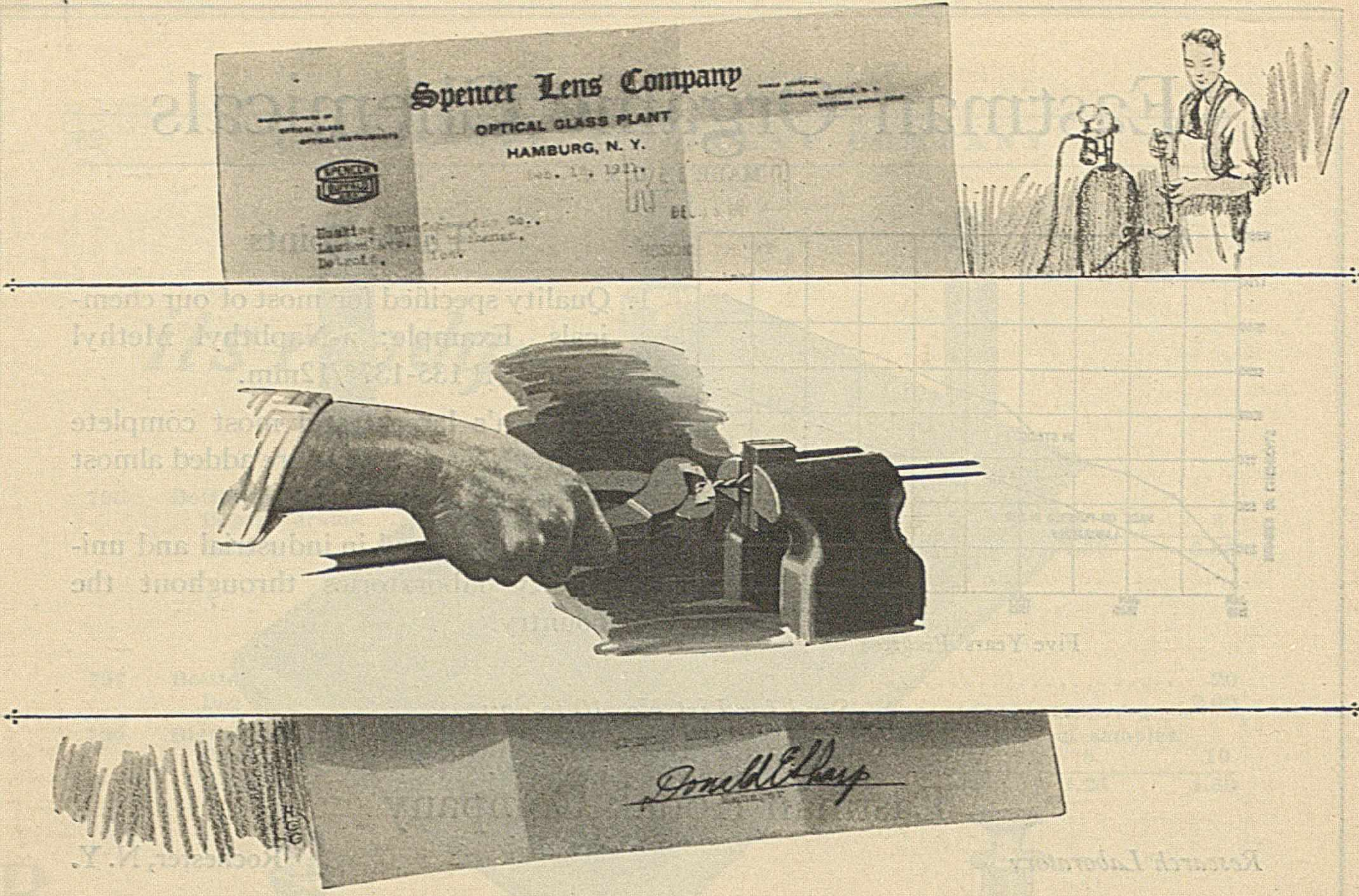

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