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EDITORIALS

Bending the Twig

THE Section of Chemical Education has appointed a committee of such importance that we should like to see it made a committee of the Council and afforded all possible assistance in the preparation of its report. Nominally, it is especially charged with correlating courses of high-school and college chemistry. As a matter of fact, it may hold in its hand the destiny of the AMERICAN CHEMICAL SOCIETY and of chemistry in America.

The progress of chemistry is necessarily dependent upon the caliber of the men who lead it, and if we are to make chemistry attractive to the best men the race produces, we must begin with the high school. If a satisfactory high-school course can be devised and generally adopted, we shall soon be sending to our higher institutions of learning these best men to be prepared for careers in fundamental research and applied science.

To devise a high-school course is a complex and difficult problem. We must not forget that we desire a sympathetic understanding of chemistry and chemical problems, even by those men who never intend to practice the profession. There are still many men who for one reason or another cannot or do not continue their education beyond the high school. It does not seem feasible to separate the students for their instruction, and consequently, the ideal high-school course would be one giving those who go no further a real insight into what chemistry means to them as individuals and at the same time properly initiating those who will continue their studies. It seems certain that such a course will be one which presents chemistry as a series of problems of immediate interest to the student as an individual or as a part of our body politic. It will be the sort of course that teaches one to place a high value on the science. It will depend for much of its material upon local industrial activities, the relation of the science to public health and medicine, and the application of chemistry in industry as shown by motion pictures. It can easily include enough laboratory work to be an added attraction to the boy at the age when he likes to construct, to work with his hands, and actually to see things taking place before him.

We trust that the committee will also consider the great advantages that could be derived from the standardization of minimum requirements in college courses. A man who derives all his training in one locality is handicapped as compared with one who has been broadened by travel. We should like to see courses adopted such that without losing time a student could obtain his education in various parts of the country, with all that this would mean in advantage of environment, contacts, and changing experience. Several universities are paying special attention to the development of courses in which more time will be given to fundamentals and the study of humanities. And if we can seriously address ourselves to the difficult task of devising the courses mentioned, we can coöperate with such educational centers and do a wonderfully important piece of constructive work. The committee should have upon it representatives of high and secondary schools, college and university groups, together with the interested representatives of industry. If these things can be brought about, we may expect before long great forward strides in chemistry in America, due to the native ability and thorough training of the men identified with the science.

"A Rose by Any Other Name—"

WE all realize the value to ourselves of the "good name which is rather to be chosen than great riches;" that is, in an abstract way we realize it—yet, when it comes to the matter of lending that good name to someone else, its value seems to dwindle in our own estimations as compared with the possibility of helping some worthy cause. In other words, our present-day ideas of service to humanity far outweigh our innate caution. Our desire to help the struggler is properly paramount, yet improperly so when it involves us in another's schemes of which we are ignorant.

During the past month our attention has been called to an organization of decidedly questionable character whose publicity teems with the names of men of national and international reputation. By sending its prospective dupe literature with such names attached, it builds up a position of secure confidence which no amount of adverse experience will serve to destroy. Among the names used by this particular organization were those of several prominent members of the AMERICAN CHEMICAL SOCIETY, to whom we wrote for information about it. What was our surprise to find that with a single exception these gentlemen knew nothing of the organization beyond the fact that they were in some way connected with it! The single exception had requested some months ago that his name be removed from its literature—which, incidentally, had not been done.

Far be it from us to cast reflections in any way upon legitimate organizations carrying out legitimate purposes in legitimate ways, but often, as in the present instance, the sweet savor of a good name is a greater temptation to the illegitimate promoter than one's pocketbook, and is often more valuable. Our government agencies have gone to great lengths to protect our cash from fraud in the form of blue-sky stock, and we owe it to ourselves to investigate the use of our name in any connection.

Earning Power of Research

IN a delightfully informal talk which Principal J. C. Irvine gave in Washington, he related a personal experience which emphasizes not only the earning power of research, but the importance of scientific publications.

Principal Irvine said that, while some might place the time at which America entered the war at a much later date, he held it to be August 9, 1914, for upon that day he received from the British War Office an urgent appeal for information on the rare sugars. This was to be expected, since Principal Irvine is a world authority on the sugars. The mobilization of the British army had created an increased demand for a number of the rare sugars which are of great importance in modern bacteriology and essential in maintaining careful watch over health. These sugars had not been produced in England and the dealers contracting with the government for their supplies depended upon foreign sources. We are proud of the fact that the work of Hudson, published in the *Journal of the American Chemical Society*, was so complete and was described with such accuracy that with but slight modifications the method was applied to commercial production. Soon England was not only supplying her own rare sugars, but exporting quantities to the European Allies for similar work.

Leadership

DISTINGUISHED foreign chemists have recently emphasized the fact that in a large measure ours is the responsibility of leadership in the world's chemistry to-day.

The history of the science in America, as it is being uncovered and established by those interested in the Section of History of Chemistry, shows that from the earliest times competent men have devoted themselves to the science here. For many decades men have gone out to the world's greatest teachers of chemistry, have been broadened by foreign travel, and returning to America, have become great teachers of chemistry. Such men, inspired by the example of older countries, have developed centers in which many a genius has had his first instruction in the science. As the wealth of our nation has increased, better and ever-better facilities for instruction and for research have been provided, until to-day our equipment is unexcelled. In many sections of the country new laboratories, built upon a generous scale, are occupied, are under construction, or have been definitely planned. Our manufacturers of equipment and apparatus are winning a very definite place and show a willingness to assist the scientist. Concurrently, our men have developed an American school of thought and method and work, and the reports of their writing have enabled our journals to earn and maintain positions in the front rank. All these developments are emphasized by those who have observed America's work from afar.

We may soon see the stream of the world's students turn toward America. There could be no better evidence that we have builded well, and no greater compliment could be paid to the success of our scientists than this tendency to entrust to their guidance selected men for graduate work!

But with this comes leadership—a serious trust—which involves sacrifice and devotion on a scale deserving all the support we can muster. We must make greater progress in the establishment of research professorships. There must be no cessation in the effort to have adequate salaries provided, both properly to recompense the men upon whose inspiration and direction the future of chemistry depends, and to insure retaining in the teaching profession the best men obtainable. These men must have equipment on a scale worthy of their ability, and there must be sufficient means for publication, without which we cannot achieve the utmost in our scientific development.

Do we want America to assume leadership? If so, each of us must realize that we have a part in the serious work which goes with it, and must be ready to meet the demands that may be made upon us.

The Automotive Industry

THE exact specifications for materials used in motor-car construction call for scientific control and supervision, and chemical research is in progress upon all features of automotive transportation. Chemistry can rightfully claim a large share in making this industry possible. The following statistics are useful in emphasizing the importance of chemistry in business:

Number of carloads of automobile freight shipped by railroad	400,000
Per cent of rubber supply used by automobile industry	83
Per cent of plate-glass supply used by automobile industry	30
Per cent of aluminium supply used by automobile industry	20
Per cent of iron and steel supply used by automobile industry	4
Gasoline consumption (U. S.), 1922 (gallons)	5,300,000,000
Gasoline consumption (U. S.), 1921 (gallons)	4,506,706,000

Proving Capability

AS organizations prove themselves capable, it not infrequently happens that funds come to them from men anxious to entrust to a group established in perpetuity the management of money for the support of worthy work. The executives of the AMERICAN CHEMICAL SOCIETY, and particularly our councilors, should keep in mind that they may be constantly on trial and that their policies, procedures, and decisions may indicate to some watchful trustee whether or not the AMERICAN CHEMICAL SOCIETY is the body to which he is justified in transferring large funds for administration. Our members are coming gradually to a realization of what a strong organization can do, not only for the advancement of chemistry, but of related sciences. Without in any way slighting the types of work for which the SOCIETY is noted, we can participate in matters of education, industry, and public welfare, and demonstrate a willingness to stand out boldly for progressive principles. Decisions should be reached only after mature consideration, and must be so sound as to win the confidence of business men who may ultimately become interested in the furtherance of our ideals.

Too few of our councilors take their work seriously. Many are inclined to hold the erroneous view that, after all, others have the responsibility for what is done. Our local sections have many opportunities to demonstrate the value of chemistry in civic and state affairs, and through their councilors they can exercise a potent influence upon the activities of the SOCIETY as a national institution. The AMERICAN CHEMICAL SOCIETY is better able than any other organization to administer funds in an impartial manner for the advancement of chemistry in its relation to other sciences, to industry, and to the nation. If we are businesslike in our own affairs, we venture the prophecy that the SOCIETY will eventually be entrusted with the administration of many important funds.

A Reasonable Request

THE Secretary of Commerce, ever alert to maintain the productivity and employment of the nation, has circulated a letter calling for coöperation on the part of the public at large in assisting in the efficient operation of our transportation lines, particularly the railways. Undoubtedly, we "can make a tremendous contribution to the orderly march of our prosperity," if the coöperation sought is undertaken seriously and in organized fashion.

In 1922 the railways of the country actually expended $440,000,000 for cars, locomotives, trackage, and other facilities, and for 1923 have authorized expenditures for equipment and other facilities reaching approximately $1,100,000,000. This in itself indicates the willingness of the roads to provide the service desired, and Secretary Hoover asks the public to assist in the following principal directions:

1—The advance storage of their winter coal during the light-consuming season—that is, from now until September 1—including the early movement of lake traffic.

2—The loading of all cars to full capacity, their prompt loading and discharge.

3—Reduction of reconsignment shipments and restriction of to-order bills of lading.

4—Demands for no more cars from the railways than can be promptly used.

It is somewhat surprising to find that if maximum efficiency can be secured in these several directions "we will have added more efficient commodity movement than would be brought about by the addition of approximately 300,000 cars and 3000 locomotives and the addition of at least 10 per cent to the

track mileage and terminal facilities." It has long since been demonstrated that we must have uninterrupted communication and transportation if production and consumption are to maintain a satisfactory relationship. Anything which interferes has an immediate effect upon price levels, and all of us, whether as individuals or members of industrial groups, are directly concerned. The requests made are eminently fair and reasonable. We urge upon our readers such unity of action as will contribute directly to continued and increasing prosperity.

Supporting Foreign Publication

IN times past we have heard much of the superiority of publication in certain foreign countries, particularly with respect to quantity. This is usually attributed to subsidies from governments or industries, but certainly at present those of us who support these foreign journals appear to be benefactors on a rather large scale.

In the January 26 number of *Chemistry and Industry*, Sir William J. Pope calls attention to the prices of German periodicals, and points out that even in June, 1922, an English member of the German Chemical Society was paying forty times as much in gold values for the *Berichte* as were the German members. In December, 1922, the foreigner paid ninety times as much for *Liebig's Annalen* as did the German. And while only one-thirteenth of the members of the German Chemical Society reside outside Germany, a simple calculation shows that this small fraction is contributing eight times as much in gold to its publication activities as are the home members.

The following list will enable one to get some idea of the comparative domestic and foreign prices of some of the leading German publications. The fluctuation of the mark, however, has made these prices far from constant, and the figures given should be regarded as merely indicative, since they vary greatly from month to month. It is interesting that such journals as are published by commercial concerns are more nearly consistent in their domestic and foreign charges than are those supported by chemical societies, but even in this case we are being asked to pay a sum quite out of reason.

	Domestic		Foreign	
	1922	1923	1922	1923
Berichte	110 mk.	...	$10.00	$10.00
Chemisches Zentralblatt	1000	...	11.00	11.00
Brennstoff-Chemie	120	2000 mk. (quarterly)	...	1.20
Mitteilungen aus dem Materialprüfungsamt	120	...	...	4.80
Petroleum Zeitschrift	400	20,000	10.00	10.00
Papier-Zeitung	200	6400 (quarterly)	...	(yearly) 4.00
Papier-Fabrikant	1500	3000 (monthly)	2000 mk.	(yearly) 4.00
Textilberichte	300	5000	1000	6.00
Zeitschrift für Elektrochemie	3000 (November, 1922)	12,250 (quarterly)	$4.00 (November, 1923)	5.00

At present there is a notable tendency on the part of German publishers to advance domestic prices. This advance has undoubtedly been occasioned by the criticism in England and the United States, but we have no data on the possible rebate to nationals. In a letter to our Committee on the Importation of Foreign Books, the president of the Deutsche Chemische Gesellschaft makes it clear that their policy is based primarily, not on cost, but on the supposed value to the subscriber and in proportion to his means. This would seem to be rather a socialistic standpoint.

As an equitable basis of exchange it has been proposed that one journal of the American Chemical Society be offered for a single German periodical, but the suggestion has not met with favor abroad.

Industrial Excursions

LOCAL sections can make a valuable contribution by furthering the interest of advanced students in the part chemistry plays in the work of the world. One way to do this is to assist them in visiting industrial plants where the raw materials used, the processes employed, the control exercised, or the development work in hand emphasize chemistry to such a degree as to give an object lesson. A strong, representative committee in each section should seriously undertake to ascertain those manufacturing establishments within a reasonable radius of section headquarters where these conditions are met. The officials of such plants should be approached, the project explained, and interest secured. Perhaps these officials have not known that their factory held any attraction for scientifically minded folk. A special effort should be made to secure the coöperation of manufacturers who have heretofore been disinclined to open their doors. Tabulated information constituting the report of such a committee should set forth any special restrictions for a given establishment, and should be prepared in sufficient detail for the use of instructors, who in turn should be urged to take classes upon these instructive tours. Such a report would be of further use to those groups of students which often travel far to see some process in operation by furnishing in advance much of the detail difficult to arrange by correspondence.

But the committee's work would not cease here. Frequently, members of the committee are best qualified to conduct a party on an inspection tour. Little time would be required, the experience would be found interesting, and the service performed really valuable. This is only another phase of our effort to acquaint as many people as possible with what chemistry does. Perhaps in this simple manner we may also do something toward breaking down what still remains of the antiquated "secret" process wall. We trust the suggestion will appeal to our local-section officials.

Suggestions for Research

THE American Electrochemical Society is to be congratulated upon the publication of a list of suggestions for research. The mere listing of such problems is often of great assistance in stimulating interest and is a primary step in active work upon pressing questions. We quote the list here and should be glad to add to it, from time to time, ideas for other worth-while work awaiting attention.

Electrolytic deposition of brasses and bronzes
Hydrogen-potential measurements of aqueous electrolytes
Electrochemistry of concentrated solutions
Electrolytic production of organic compounds
New uses for chlorine and caustic
Electrolytic production of lithium hydrate
Studies of the properties of the alkaline-earth alloys
Effect of impurities in the electrolysis of fused magnesium salts
The electrochemistry of gaseous conduction
Electrical conductivity of metals and alloys above melting point
Stability of the metal carbides at elevated temperatures
Revised melting-point determinations of refractory oxides, pure and commercial
Stability of the metal silicides at elevated temperatures
Energy losses in electric furnaces
Gaseous reduction of metal compounds
Equilibria studies in electric steel furnaces
Putties and cements used in electrochemical industries
Electrical porcelain
Dielectric constants of mineral oils
Dielectric constant *vs.* composition of glasses
Dissociation of compounds in the Beck arc
New uses for iodine electrolytic production of iodine compounds

NEW HAVEN MEETING

There had never been any question but that the 65th meeting of the American Chemical Society at New Haven during the week of April 2 would be upon an unusually high plane. It was also certain that the unusual features announced would be sure to attract many of our leading chemists, and these men themselves afforded an attraction which brought together an attendance well above 1500. A number of chemists arriving on Thursday and Friday failed to register.

One of the very enjoyable outstanding features of the meeting was its delightful international aspect. Foreign chemists representing England, Scotland, France, Italy, Holland, Sweden, and Canada came at the special invitation of Yale University and delivered addresses of great interest to several special groups. These visits were made possible by friends of Yale, and it is hoped that a precedent has thus been established whereby friends of science in the various localities where our Society meets can make it possible for one or two prominent international scientists to attend future meetings. If the presence of foreign scientists at our meetings is stimulating, it is no less true that our own leaders owe it to the younger men and to the advancement of chemistry to attend Society meetings, deliver papers, and take a leading part in the discussions. Many of the men missed in recent meetings were in attendance at New Haven.

The State of Connecticut and the City of New Haven did all they could to contribute to the success of the meeting. With the presence of noted men and the unusually high quality of papers presented, there stands out as a feature of the meeting the dedication of the Sterling Chemistry Laboratory. This laboratory was described in the March issue of This Journal. The dedication exercises were conducted in the industrial laboratory, and the procession of dignitaries, led by President James R. Angell and President-Emeritus Arthur T. Hadley of Yale, presented an impressive and colorful sight as they entered the auditorium clad in their academic robes. The Sterling Laboratory is a bold experiment in design and construction, which demonstrates that a monumental building can be adapted to laboratory uses. Remembering the epoch-making work of the early chemists of Yale, with little encouragement and meager equipment, with the facilities now available, chemistry can properly look to Yale for accomplishments of the first magnitude.

The Council Meeting

The Council, composed of 6 general officers, 8 past presidents, 8 chairmen of divisions, 6 councilors-at-large, and 112 local-section councilors, of which 31 were substitutes, met on Monday. On Wednesday a special meeting was held.

Resolutions on the death of E. W. Morley were presented by O. F. Tower and unanimously adopted. Certain historical papers in the possession of the Society were added to the historical collection of Edgar F. Smith. A. W. Brown, of Cornell, extended an invitation for the Society to meet in Ithaca in September, 1924. A new section, to be known as the Erie Section, at Erie, Pa., was granted a charter, and approval was given for the formation of a tri-city section covering the territory of Rock Island, Clinton, and Moline, Ill. The announcement was made that Swift & Company has added a fellowship to the list of those created for chemical research. A. M. Comey was elected to the Committee on National Policy (Advisory Committee) to succeed George D. Rosengarten.

The motion to reverse the action of the Advisory Committee on the Stanley patent bill was defeated by a decisive majority. The real point at issue was not so much the Stanley bill itself, since that proposed legislation went into the discard with the adjournment of the last Congress, but was whether the Advisory Committee had exceeded its authority in speaking for the Council. Reference to the action in 1917 creating the Advisory Committee made it clear that it is to speak for the Council between regular meetings, and the vote taken affirmed that action.

At the second meeting of the Council, the report of the Committee on Progress in Society Procedure was considered first by the Council as a committee of the whole and then reported by the committee to the Council itself, thus affording two opportunities for complete discussion. The Council approved the general plan of regional representation of directors, and instructed the Advisory Committee to determine territorial boundaries to afford equitable representation and to submit a plan, together with proposed changes in the by-laws, to make such plans effective at the next Council meeting.

It was voted that the Advisory Committee be changed to an Executive Committee of the Council with the powers previously given the Advisory Committee and also the usual functions of an executive committee. The Advisory Committee was asked to recommend the personnel of this committee, and report to the next meeting.

The Council further voted that the size of the Council be reduced, and that the Advisory Committee recommend upon what lines this reduction be made. It was suggested that in the future, in order to allow ample time for the conduct of the Society's business, no complimentary dinner be extended to the Council, but that both afternoon and evening of the first day be made available for Council meetings.

The President, as authorized by the Council, appointed a committee, William Hoskins, chairman, to report at the next meeting on methods whereby an enhanced value may be placed upon membership in the American Chemical Society. A second committee, M. T. Bogert, chairman, was appointed to consider and report upon a plan for making intersectional meetings official and to advise upon whether or not such meetings should take the place of the spring meetings of the Society.

The minority report submitted by H. C. Parmelee was received and placed on file with the thanks of the Council. Mr. Mory's committee was heartily thanked and discharged, and those responsible for the success of the New Haven meeting given a sincere vote of thanks. Upon the recommendation of the chairmen and secretaries of divisions, the Council passed a recommendation that the Secretary of the Society be instructed to mail the final meeting program not less than ten days before the date of the Council meeting and that the final date for the acceptance from authors of titles and abstracts of papers, by secretaries of divisions, be set at least one month before the date of the Council meeting. This is unquestionably a progressive move and it is hoped that it will result in the papers being themselves submitted in sufficient time before the meeting to permit their careful consideration.

The New Haven meeting goes into history as one of the most successful held by the Society, and sets a high standard which our future meetings will do well to emulate.

The History and Status of Chemistry in Petroleum Research

By Carl O. Johns

Research Division, Development Department, Standard Oil Company of New Jersey, Elizabeth, N. J.

PETROLEUM has played an important role in the history of many races of mankind. It was used to make mortar in the building of the tower of Babel and the ancient records of China and Japan contain references to petroleum. Natural gas was employed by these peoples for fuel and light before the Christian era.

The use of petroleum is mentioned a number of times by the old classical authors, and Herodotus, writing about 450 B. C., tells us that bitumen was used as mortar in building the walls of Babylon.

The oil springs of the Caucasus have been known since ancient times, and Marco Polo, the famous Venetian traveler, writing at the end of the thirteenth century, states that "On the confines toward Georgia there is a fountain from which oil springs in great abundance and a hundred shiploads might be taken from it at one time. The oil is not good to use with food, but is good to burn, and is also used to anoint camels that have the mange." Natural gas constituted the Eternal Fire of Baku, the principal city of the Fire-Worshippers.

Carl O. Johns

What is probably the first printed reference to the refining of petroleum on the Pacific Coast (Peru) of this continent appeared in 1569 in a book entitled, "De Las Drojas De Las Indias." This book was translated in 1596 by John Frampton, in London, who gave it the title "Joyfullnewes Out of the New-Found World."

In 1723 Peter the Great of Russia wrote to General Matushkin, who was then stationed at Baku, to send him one thousand poods of white petroleum and also to find a man who understood how to refine it. This indicates that attempts at refining had been made previous to this time.

The art of distillation was practiced by the ancient Egyptians during their long and highly developed period of civilization, and the alchemists of the Middle Ages made use of the still in their endeavors to find the elixir of life. It is not strange, therefore, that distillation was employed early in refining petroleum for medical purposes. It is certain that petroleum was distilled in Russia in the eighteenth century and probably earlier, for Johann Lerche, who visited the Caspian district in 1735, found that the crude Caucasian oil required distilling to make it satisfactorily combustible, and that when distilled it yielded a bright yellow oil resembling a spirit, which readily ignited. As early as 1823 the Dubinin brothers erected a refinery in the village of Mosdok. This is said to be the first attempt to make kerosene from petroleum.

In 1846 Prince Woronzoff sought the aid of the Caucasian government in extending the use of petroleum distillates. In his petition he describes the use of an iron still set in brickwork, and from a working charge of forty "buckets" of crude oil he obtained a yield of sixteen "buckets" of white naphtha. The top of the still had a removable head connected with a condenser consisting of a copper worm in a barrel of water.

About the year 1850 Baron Thornau built a plant for refining Russian petroleum. Thornau seems to have had unusually good sense, for in his undertaking he sought the advice of the famous German chemist, Justus von Liebig, who furnished plans for the refinery and sent one of his assistants to aid in its erection.

The beginning of the petroleum industry in the United States may be said to date from about 1826, when Dr. Hildreth visited the oil springs of Ohio and reported that petroleum had great possibilities as an illuminant. A little later Seneca oil and American medicinal oil were put on the market and widely advertised as sure panaceas for most human ills.

As early as 1833 Prof. Benjamin Silliman, Sr., of Yale College, had made a number of distillations of petroleum in glass retorts, and he found that the distillate was light in color and the residue was thick like pitch.

In 1854 the Pennsylvania Rock Oil Company was formed for the purpose of procuring surface oil near Titusville, Pennsylvania, by the method of digging and trenching. One of the prominent men in this company was Mr. George A. Bissell, of New Haven. A sample of the oil obtained in this venture was submitted for analysis to Prof. Benjamin Silliman, Jr., of Yale College. Professor Silliman made his report to Messrs. Eveleth, Bissell, and Reed on April 16, 1855. This document is a classic on the chemical technology of petroleum, and represents one of the most important researches in industrial chemistry that has ever been undertaken. Since this gathering represents not only one of the national meetings of the American Chemical Society, but is also the occasion of the dedication of the new Sterling Chemistry Laboratory of Yale University, it seems appropriate to discuss briefly the contents and importance of Professor Silliman's report.

Professor Silliman's Report

Professor Silliman states that the sample of oil which was given him for analysis had a dark brown color with a green or blue fluorescence. When it was exposed for a long time to the air, it did not form a skin on the surface, and for this reason could not in any way be regarded as a drying oil. The specific gravity of the oil was 0.882. It gave off vapors at temperatures slightly above the boiling point of water. It took fire with difficulty and burned with a very smoky flame. Between the fingers it felt slippery and fatty. Chemically, it differed from the fatty oils. Naturally, the question was—what commercial value did it have and what use could be made of it. Silliman's investigation gave the answer to this question.

The oil was distilled into fractions in order to find out what products might be obtained therefrom, and the temperature was carefully noted by means of a centigrade thermometer during the distillation. The heating was first carried out by means of a water bath, then by a bath of linseed oil. The lighter fractions were light in color, while the heavier fractions were dark and

had a strong empyreumatic odor. The specific gravities of the different fractions were found to range from 0.733 to 0.7854.

On redistilling these fractions Silliman noticed that they began to boil below their original initial boiling points, and that the end-points were very much higher than the original. He states that the variation in the boiling points showed that these distillates contained a mixture of many different products, and he brought up the question as to whether or not these products existed in the original crude or were formed by chemical changes during the distillation. He says that temperature alone is sufficient to change the constitution of a large number of organic compounds and to produce new compounds which are not present in the original substance.

After the first distillation all fractions contained a very small quantity of free acid. This acid could be removed with weak alkali and water, or by simply boiling with pure water. The distilled oil did not attack clean copper, which showed the absence of corrosive properties and therefore indicated that it could be used for lubrication. It did not contain oxygen and had no effect on clean potassium. It decomposed strong sulfuric acid, which likewise decomposed the oil. Nitric acid changed it to a yellow, oily liquid. Hydrochloric, chromic, and acetic acids did not change the oil. Metallic oxides did not convert it to a drying oil. It did not attack potassium at a high temperature. Potassium, sodium, and calcium hydroxides had no action on it, nor had calcium chloride or other salts. When distilled with chloride of lime it gave a product which resembled chloroform.

The oil was investigated to ascertain if it could be used for the manufacture of illuminating gas. An almost pure hydrocarbon gas of the highest illuminating power was obtained. He states that one can, in fact, regard the oil as chemically identical with light in a liquid form. Ten cubic feet of gas were obtained from one pound of oil. This gas burned with an intensive flame and smoked with an ordinary gas burner, but gave a very pleasing flame with the Argand burner.

Distillation at higher temperature was carried on in a copper retort which held from five to six gallons. The heat was raised rapidly to about 280° C. It was finally carried up to 390° C. (750° F.), and in order to get this temperature it was necessary to heat the retort with dry walnut wood. When the last fraction was cooled, there was obtained a thick mass of pearly crystals which were paraffin. These crystals could be separated and obtained as a white substance and from it beautiful candles could be made. Silliman believed that the paraffin did not exist as such in the original oil, but was the result of the high temperature during the process of distillation which caused a new arrangement of the elements. Silliman also distilled his oil with superheated steam.

The result of the various distillations at higher temperature gave a yield of over 90 per cent of the whole product, consisting of a series of oils with valuable properties which seemed to be useful for illuminating and lubricating purposes. A second distillation of a part of the higher fraction which had been distilled at 343° C. gave a thin oil with a specific gravity of 0.75. About 50 per cent of the crude oil could, by distillation, be used for illuminating purposes without any further treatment than the simple purification of boiling with water.

Silliman made a systematic investigation of the distillates that he had obtained for the purpose of ascertaining their illuminating value. In this investigation he made use of the various kinds of lamps which were then available in order to obtain the intensity of the illumination produced. At that time gas sold in New Haven at four dollars per thousand cubic feet and whale oil for two dollars and fifty cents a gallon. The distillate which Silliman obtained from his petroleum gave a better light than any other substance which was used for illumination at that time.

Silliman's report not only brought out the economic value of petroleum, but furnished information on the chemistry of petroleum which is of fundamental importance in modern refinery practice.

Notwithstanding the information furnished by Silliman, the Pennsylvania Rock Oil Company was not successful, because the cost of obtaining the crude oil was too high. Mr. Bissell was, therefore, left with the Titusville property on his hands. However, in 1857 he conceived the idea of *drilling* through the rock for oil in the same manner as that used in drilling for brine. He did not have the necessary capital to carry out his idea and therefore formed a small syndicate in New Haven to work the Titusville oil lands. Edwin Laurencine Drake was appointed director of the work. The result was the drilling, in 1859, of the Drake well, which yielded about twenty-five barrels of oil per day. The success of this venture spread like wildfire and in a relatively short time drilling operations became common and there was a large production of oil. This oil, however, would not have had any appreciable economic value had it not been for the fundamental researches made by Silliman, which laid the foundation for a process of refining it and showed the important uses of the products.

From the small production of the Drake well the American oil industry has grown so that in the year 1922 the United States produced 551,197,000 barrels, or 64.7 per cent of the world's production. Mexico, largely through American initiative, also contributed 185,057,000 barrels, or 21.7 per cent of the world's output, making the total production for the United States and Mexico 736,254,000 barrels, or 86.4 per cent of the world's output for the year 1922.

Recent Research

Since the days of Silliman, petroleum research has lagged behind the rapidly growing industry. This is partly due to the manner in which the industry has developed. For many years the manufacturing problem was comparatively simple. The principal products of the refinery were kerosene, lubricating oil, and paraffin wax. Gasoline was then a by-product for which but little use could be found, and most of it had to be wasted. There was, therefore, no incentive borne of necessity in the industry for research of a fundamental nature.

The first serious chemical problem of the industry came without warning when the Lima oil of Ohio was discovered. This oil could only be used for fuel purposes on account of its high sulfur content and its terrible odor. Canadian oil was of the same type. The problem of refining these oils was finally solved by Herman Frasch, who found that the sulfur and vile smells could be removed by heating the oils with copper oxide during the process of distillation. The researches of Frasch increased the value of these oils about seven-fold almost immediately.

Petroleum research has attracted a relatively small number of chemists compared with the large army that has been engaged in research on coal tar and its derivatives. Nevertheless, the scientific investigation of petroleum has not been entirely neglected. During the last fifty or more years there have always been one or more of a small group of American chemists engaged in fundamental research on petroleum. Among these pioneers in the United States are Warren, Mabery, and Coates. The published work of these men and their co-workers has given us most of the information which we have on the chemistry of American petroleums and also to a considerable extent on foreign petroleums. Professor Mabery has lately been at work on an investigation of the nondistillable fractions of petroleum. Considerable work has also been done abroad, especially in England, Germany, and Russia.

The results of these investigations reveal that petroleum is composed almost entirely of hydrocarbons, but of several different series. Our knowledge is chiefly confined to fractions boiling below 120° C., although certain individual compounds have been isolated from the large number existing in the fractions boiling between 120° and 300° C. Very little is known concerning the compounds in the fractions with higher boiling points.

Composition of Petroleum

The chemical composition of petroleum varies greatly with the region in which the oils are found. It is possible to give here but a very brief review of the compounds which have been isolated.

Paraffin Series (C_nH_{2n+2})—Compounds of this series are found in the lighter fractions of almost all petroleums. Nearly all the members of this series, including many isomers, from methane to nonane, have been isolated from various types of light petroleum distillates. These, with the exception of methane, ethane, and propane, are present in and constitute the major portion of gasoline. They are also found in natural gas, and this is the source from which they may be most easily fractionated in commercial quantities. Five isomeric hexanes have been found in petroleum—normal hexane, methyldiethylmethane, diisopropyl, propylisopropyl, and trimethylethylmethane.

At least six heptanes have been identified. Only two of the many octanes have been isolated, and the same is true of the nonanes. In fact, we know but little concerning the composition of the paraffin fractions having boiling points higher than the heptanes. This means that most of our knowledge is limited to the paraffins constituting gasoline, the average molecular weight of which is about that of octane. If we assume that the average yield of gasoline from crude petroleum is about 20 per cent, we are faced with the fact that the composition of the remaining 80 per cent is almost unknown.

Olefin Series (C_nH_{2n})—Members of this series are also said to be present in small quantities in some petroleums. Engler, however, seems to think that olefins do not exist in crude oils, but are formed during the distillation. Among the olefins which have been isolated from petroleum distillates are hexylene, heptylene, octylene, a nonylene of unknown constitution, decylene, tetradecylene, and some others of unknown constitution. Distillates made by the cracking process may contain high percentages of the olefins. The same is also true of distillates made from shale oil.

Acetylenes (C_nH_{2n-2})—That these compounds may be found in petroleum distillates is indicated by the isolation of hexadecylacetylene from an Ohio oil.

Benzene Series (C_nH_{2n-6})—This series is well represented in a number of different petroleums from various parts of the world. Among the compounds of this series which have been isolated are benzene, toluene, the three xylenes, mesitylene and pseudocumene, ethyltoluene, durene, and isodurene, diethyl benzene, *m*- and *p*-cymene, diethyl toluene, isoamyl benzene.

The dicyclic and tricylic compounds, naphthalene and anthracene, and some of their derivatives have also been found in petroleum.

Cyclo Paraffins or Polymethylenes (C_nH_{2n})—These compounds are present in a variety of oils from different parts of the world. They are called "naphthenes" by petroleum chemists. Among those isolated from different petroleums are cyclopentane, methyl cyclopentane, dimethyl-1,1-cyclopentane, dimethyl-1,3-cyclopentane, cyclohexane, hexahydrotoluene.

A number of other hydrocarbons of this series, such as cycloheptane, cyclo-octane, and cyclononane, and derivatives of these have been isolated, as well as many similar compounds of unknown constitution, which have the general formula C_nH_{2n} and probably belong to this series.

The heavier lubricating oils are supposed to consist mainly of cyclic compounds of the general formulas C_nH_{2n-2}, C_nH_{2n-4}, C_nH_{2n-6}, up to C_nH_{2n-20}. The heaviest oils contain compounds of very high molecular weights. Mabery has recently made an extensive investigation of such oils and has found compounds or groups of compounds of such general formulas as C_nH_{2n-8} and C_nH_{2n-20}, represented, respectively, by $C_{122}H_{236}$ and $C_{122}H_{224}$, or molecular weights of 1700 and 1688. The determination of the constitution of compounds of such high molecular weights is no simple problem.

Sulfur—Sulfur occurs in petroleum in a free state, as hydrogen sulfide, or in combination with carbon and hydrogen. Mabery has made a study of the sulfur compounds in Canadian and Ohio oils, and from the Ohio oils he isolated a series of compounds of the general formula $C_nH_{2n}S$. $C_8H_{16}S$ and $C_{18}H_{36}S$ are examples of this type of compounds. Alkyl sulfides, such as ethyl sulfide, $(C_2H_5)_2S$, are also found, and a number of these have been isolated. There are present also other sulfur compounds which have not been isolated and which do not give reactions characteristic of the thiophanes or alkyl sulfides.

Nitrogen—Nitrogen is present in petroleum from traces up to 1.5 per cent. California oils contain a relatively high percentage of nitrogen. This exists in basic compounds that have an odor and some other properties resembling the pyridine bases. Mabery has shown that if the average composition of these bases is $C_{10}H_{13}N$, some California oils might contain from 10 to 20 per cent of pyridine bases.

Oil-Cracking Processes

Although Silliman discovered, as early as 1855, that petroleum can be cracked, the first cracking process which was successful in producing gasoline on a large commercial scale was that worked out by Dr. Burton and his associates, of the Standard Oil Company of Indiana. This process consists essentially in heating gas or fuel oil under a pressure of about ninety pounds per square inch. This process has been so successful that through its use 750,000,000 gallons were produced in 1920. A more recent process of cracking, developed by the Standard Oil Company of New Jersey, is known as the "tube and tank" method. In this process the oil is heated in tubes and then transferred to insulated steel tanks, where it is kept at a high temperature and pressure for a sufficient length of time to allow the necessary cracking to take place.

All the cracking processes now employed for making gasoline produce a considerable quantity of fixed gases, which consist of saturated and unsaturated hydrocarbons. Working under assigned patents the Standard Oil Company of New Jersey has developed and is operating a process of making higher alcohols from the olefins that are found in these fixed gases. Among the alcohols produced by this method are isopropyl, secondary butyl, secondary amyl, secondary hexyl, together with small quantities of other higher alcohols. The laboratory researches which have been made on the chemical constitution of these alcohols indicate that they are all normal chain alcohols with a hydroxy group on the second carbon atom. This development has placed on the market a series of higher alcohols, all of which have hitherto been exceedingly rare, and as a result a number of these have already found important commercial uses.

Dr. Ossian Aschan, of Finland, has also produced higher alcohols on a laboratory scale by chlorinating paraffin hydrocarbons, changing the chlorides to acetates, and then hydrolizing the acetates. In this way he has obtained a number of higher alcohols from petroleum. This process, however, is probably too costly to find commercial application.

POSSIBILITIES OF PETROLEUM RESEARCH

The courses in organic chemistry given in most of our universities devote but little time to the petroleum industry. A well-known textbook on organic chemistry which is used internationally allocates but two of its six hundred pages to the subject of petroleum. The industry needs a systematic study of the chemical composition of petroleum such as has been made of coal tar during the last fifty years. The problems, however, are of far greater complexity than those encountered in the investigation of coal tar.

Petroleum affords a veritable mine of organic compounds. The magnitude of the industry is such that petroleum research should attract the best trained organic and physical chemists in our universities. Who can predict how far reaching both from economic and scientific aspects would be the results of a thorough scientific investigation of this almost virgin field?

The Chemist Enters a New Industry[1]

By H. E. Barnard

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FIVE or ten thousand years ago a primitive baker pounded up a handful of cereal grains, wet the mass, and baked it on a hot stone. In the course of centuries he improved his process somewhat. He sifted his flours, he arched his hot hearthstone. One day he made up too large a batch of dough and left some of it unbaked. After the manner of dough, it became food for yeasts and fermented. The next bake was leavened bread, and after years of casual handling of sour dough, yeast-raised bread became the basic food of most civilized people. But after thousands of years of skilful craftsmanship bread baked but a few decades ago was made in the same way as it was in the valley of the Nile when King Tut was put into storage; as it was when the bakers of Pompeii fled before the descending ashes of Vesuvius; as it was when our Puritan ancestors poached the Indians' corn cribs and made the first New England johnny cake.

H. E. BARNARD

Is it safe for me to say here within a stone's throw of all the world's history entombed on Yale campus, that baking science has developed more in the past ten years than in all the previous years of man? And dare I say that a few baking chemists working under little appreciated difficulties have in these short years overthrown the craft control of a hundred centuries and built a scientific industry which is doing the baking of the world in great laboratories, more economically and far better than ever before?

To be sure, chemists have helped the miller buy wheat for his grinding for many years. They have more or less stupidly and empirically evaluated flour by weighing ashes and digesting proteins. They have given assistance to the brewer and distiller, turned yeast-maker for the baker. But their routine service never unlocked the secrets of fermentation nor solved the mystery of gluten. And then came the Great War and days that were wheatless and, so far as the baker was concerned, two years crowded with enough grief to make a lifetime miserable. He gave over the operation of his shop to the minions of the Food Administration. He learned that bread could be made without flour—or much of it—that there were other ways of feeding yeast than with sugar, that lard wasn't a necessity, that poor materials properly handled would make rather good bread. Then, too, he learned the need of making bread that would not get stale over night, for among the hampering rules of war time was one that made bread stay sold. Once it reached the grocer it went on to a customer—not back to the shop the next day, if it was unsold. Out of the chaos which confronted every baker emerged an industry with a vision of the value of science, of the need of the chemist in the shop. To be sure, the vision was focused on practical things—on better buying methods, on relative values of materials, on the fitness of shortenings, sirups, sugar, and salt for their particular purpose. But fortunately, a chemist once installed in a laboratory is like a camel's nose under a tent. Before long he makes the whole plant his laboratory.

So it has been at the bakery. To-day, the making of bread is a chemical process with physical and biological aspects, carried out in huge laboratories filled with automatic machinery operating under temperature, humidity, and time control.

And here is where my story begins. Come with me to this newest of industrial laboratories where a new school of chemists makes its daily bread. All materials are bought on specifications. Flour brands mean nothing except in their ability to produce a good loaf of bread. In other words, such flour conforms to the standards of gluten quality, which measures strength; of ash content, which is the gage of milling efficiency; of moisture, which so influences the absorption of water-carrying capacity and which is much cheaper when drawn from a tap at the bakery than when freighted half-way across a continent in a flour sack; of color, which means high milling standards, or bleaching, or both; and of hydrogen-ion content, which some chemists believe is a better indication of flour maturity and adaptability for successful use than high protein or low ash.

Milk is an essential ingredient of modern bread. From a nutritional viewpoint it plays a role second only to that of flour itself. And every month—for we measure developments in baking chemistry by months now, instead of years—more milk is going into the formulas. What kind of milk comes into the stock room? What is its fat content, its acidity, its sugar content? And is the salt worth its cost? Is there any ground for the salesman's argument that his particular salt is sweeter than competing brands and that the baker can use more of it?

Are the diastatic malt sirups really diastatic, and how much? What about the yeast foods—do they contain talc? And the shortenings—are they true fats or doped mixtures of glycerol, alum, starch, and water? Is the yeast alive and eager to populate the dough batch with its virile progeny, or is it weak and

[1] Presented as "The Baker Turns to the Chemist."

unwilling to work? Of course, most of these chemical controls of materials are not new; it is their application in the bakery that commands the chemists' attention. And when the chemist has checked up his bread ingredients he has the usual line of work still to do—fuel for the ovens, lubricating oils and grease, paints, oils, varnishes, soaps, and washing powders—all old jobs for routine workers.

But chemical control goes beyond the analytical laboratory. I mentioned hydrogen-ion determinations on flour samples. What business has a hydrogen ion in a dough batch? Here is where the chemist lays aside his apron and puts on his baker's cap. Dough is flour, water, salt, yeast, plus milk, sugar, shortenings—all the materials bakers use to make good bread. For centuries the yeast-planted dough was allowed to ferment for hours. Most homemade bread is fermented over night, on a chair by the kitchen stove. Usually a red shawl is thrown over the dough pan. If the night is cool the dough doesn't rise very well and mother has it in for the miller and buys another brand of flour next time. If the night is hot then the yeast gets busy and lifts the dough mass over the side of the pan. In good bakery practice the dough comes out of the mixer at a definite temperature and stays in the fermentation room, with occasional punching to release the imprisoned gases of fermentation, from three to five hours, the time element depending on room temperature and flour or gluten quality and other less influencing conditions. What is the reason for this long fermentation period? Bakers say "It's to mature the gluten." What does that mean? It took a chemist to answer a simple question that had remained unanswered from the time the first dough was punched until a few years ago when Jessen Hansen, working under Sorensen at the Carlsburg Laboratories, began to study hydrogen ions and applied them in the measuring of flour and dough acidity. Gluten is an extraordinary material. Flour strength depends on its gluten content, and even more on the character or quality of the gluten. But even the best of glutens will not entangle carbon dioxide in just the way to give ideal texture and grain to the finished loaf unless it is treated right—"softened," the baker says. And it's the lactic acids and other acids which are formed while the yeast is working away in the dough room which soften gluten.

Here enters the chemist again, hydrogen electrode in hand. "Why not," he says, "find out just how much acid it takes to mature or soften or make just right the gluten of this particular dough batch?" And he does it—and then, instead of training and coddling a trillion or so yeast plants to develop the proper acidity, he puts the calculated amount of lactic acid, or whatever acid salt he finds most useful, into the dough mixer, develops the gluten as best he can by physical means in his high-speed mixer, and shoots the well-mixed dough out of the mixer down to the divider to be cut into uniform sizes for the desired loaf. And it never goes into a dough trough or stops for a moment in the dough room. Four hours taken out of the baking process, and the trough out of the equipment.

This isn't a secret process, not quite. At the American Institute of Baking we have been studying the effect of acids and acid salts on panary fermentation for nearly three years, and our students are taught how to make so-called "quick" or lactic acid doughs. But the process is just coming into bakery practice. I recently asked the technical head of one great baking company how he proposed to teach his bakers how to make hydrogen-ion determinations and apply them to the doughs in the form of cubic centimeters of acid or grams of salts, "That's easy," he said, "we shall not have any bakers in the shop." And when I asked him who was going to make the bread he said, "The shop chemist, of course."

Well, that seems to be about the end of my story. The chemist has taken over the steel mills, the glass factory, the rubber works—every industry which fabricates raw material into finished products for the benefit of mankind. And now the baker has gone the way of the butcher and candlestick maker. Bread is no longer a work of art—guess work, at that—but an achievement of science, built of selected materials combined by controlled processes, with no waste of materials in the fermentation process and no possibility of a poor product coming out of the oven.

There is need of chemists for the baking industry—a greater need perhaps than in any other industry—but to the science of the classroom and laboratory must be added the practice of shop operation. And greater even than the need of chemists in the bakery is the need for research workers in a score of vital problems of the wheat farmer, the miller, the yeast maker, the malt sirup maker, and in every field which supplies the needs of the baking industry, the most important of all food industries and still the least informed.

While statistics are hard to secure and harder to listen to, it is of some interest that 60,000,000 barrels of flour are being turned to bread this year; that 33,000 bakers are hard at the task, most of them still using shoulder muscles instead of machines and craft rule-of-thumb practice instead of scientific formulas; that the value of the product is up in the billions; that the industry which ranked seventeenth in 1900 is now seventh in magnitude and growing by leaps and bounds; that home baking is passing as surely as home weaving or home brewing, perhaps more so, and that the latest baker's loaf is so perfectly balanced and built up that all it is necessary to take into the wilderness is a loaf of bread and a jug of water to satisfy at least the nutritive needs of mankind.

The complete food in pill or capsule has long been talked of. Now, our chemists have brought it to pass in the form of bread. Numerous generations of mice and rats attest its completeness by increasing their progeny with each new generation. Speculation as to the effect this astonishing loaf will have on the Malthusian doctrine is not as yet in order, for the life cycle of the human family is markedly different from that of the mice and rats who are willingly serving as subjects in these nutritional studies. In the Nutrition Laboratories of the American Institute of Baking, we have demonstrated the great nutritional advantages of the use of milk in bread formulas by feeding experiments on white rats. The average American may little need such a complete food in a single article of diet. It is worth noting, however, that chemists at the bakery can and are producing a complete ration, and that after these many years of effort the baker's oven is giving us bread that is superior in craftsmanship, in scientific uniformity, and in nutritive value to the homemade loaf.

I cannot let this opportunity pass without telling of the need at the American Institute of Baking for research fellows. Several fellowships are available for chemists who may wish to make cereal and baking chemistry their life's work, and, for other chemists who may wish to fit themselves for positions in the modern bakery, our School of Baking offers short courses which are proving entirely practical. Our only sorrow is our inability to meet the demand for chemists with the special knowledge required of them in the bakery.

Complimentary Luncheon

Following the dedication of the Sterling Chemistry Laboratory, Yale University entertained specially invited guests, ladies, and members of the American Chemical Society at luncheon in the University Dining Hall. At the conclusion of the luncheon, before introducing the speakers, President Angell briefly traced the history of chemistry at Yale. He then introduced T. W. Richards, of Harvard University, who referred to the importance of chemistry to medicine, agriculture, hygiene, and industry in peace even more than in war. The following distinguished foreign representatives were then introduced and spoke in a delightful vein, congratulating America upon the rapid progress of science here: W. Lash Miller, of the University of Toronto; Guiseppe Bruni, of the University of Milan; G. Urbain, of The Sorbonne; A. F. Holleman, of the University of Amsterdam; T. Svedberg, of the University of Upsala, Sweden; F. G. Donnan, of the University of London; and J. C. Irvine, of the University of St. Andrews, Scotland.

The Influence of Light on Inorganic Matter and Life Processes

By Oskar Baudisch

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NATURE OF LIGHT

IF WE WISH to discuss somewhat in detail the influence of sunlight upon inorganic matter and upon living processes, we must first get a clearer idea as to the real nature of light. Isaac Newton believed that the sun sends out light in all directions in the form of infinitesimal particles, which traverse space with the velocity of about three hundred thousand kilometers per second. Light, therefore, according to Newton, was something material and the velocity of light resembled that of atmospheric winds. Newton's emanation theory was combatted by Huyghens, who opposed to it the much more workable undulation theory of light. Huyghens compared the velocity of light, not with that of wind, but with that of sound. That which is transmitted by a cannon-shot in all directions with uniform velocity is not particles of air, and therefore of matter, but rather alternate condensations and rarefactions—that is to say, a certain state of matter. A familiar analogy is the phenomenon observed when one throws a stone into quiet water. The material particles, in this case particles of water, undergo a stationary vibration, whereas to the eye it appears as if there were actual translatory motion in all directions. Huyghens was obliged, in order to explain the propagation of light through interstellar space, to postulate the existence of a new medium, called ether.

Roger Sherman Studio
OSKAR BAUDISCH

About the middle of the nineteenth century, Maxwell announced the bold hypothesis that light is an electromagnetic phenomenon, and thereby rendered obsolete the old mechanistic theory of light. The success attendant upon Maxwell's wonderful ideas was astounding. Huyghen's undulatory theory remained essentially unchanged, except that in place of the ether vibrations, emanating in concentric spherical waves in all directions from the light source, we now have electromagnetic energy. With the aid of Maxwell's new ideas, the entire field of research in radiation was enormously extended and we were soon forced to conclude that what had popularly been known as light was only a small part of the radiant energy emitted by the sun and other heavenly bodies. The electromagnetic theory of light will in all probability remain unshaken, but Huyghen's undulatory or wave theory seems to be in serious danger, owing to certain facts which have been only recently discovered.

We have still to discuss very briefly the most modern theory of light due to Planck and Einstein, which invalidates Huyghen's theory. This new theory is very useful in the explanation of photochemical processes, but so far it has failed to explain certain optical phenomena. The question "What is light?" therefore is still not completely answered.

According to Planck and Einstein we think of light as that form of pulsating energy which is emitted whenever an atom disintegrates; or, in other words, light is the result of an internal cataclysm of the atom. The electrons of the atom, which revolve around a nucleus much as the planets revolve around the sun, are deflected from their original paths into others which are more stable but involve less energy. The excess of energy, which is hereby lost to the atom, rushes out into space in the form of so-called "light quanta." If a great deal of energy is emitted there is formed ultra-violet light, or even X-ray radiation; if the amount of energy emitted is not so considerable, infra-red rays are the result.

Thus it may be seen that we are approaching once more the old Newtonian theory of light, but with the vast difference that electromagnetic energy, instead of matter, is emitted from the source of light in all directions.

Heretofore we have briefly discussed the physicist's conception of light, and we must now consider what we shall mean by a chemical action of light. The answer to the question is no longer as difficult as it once was, since we know that light represents a definite form of energy. By a chemical action of light we must inevitably mean a change from radiation or light energy to other forms of energy, and it is therefore merely a special case of the general transformation of radiation. As long ago as 1818 Grotthus announced the law which asserts that a photochemical change takes place only when the radiation is absorbed by the body exposed to it. This law is still valid, in spite of all subsequent changes in the different theories of light. Of course, the light which is absorbed by the body does not have to perform exclusively chemical work. In fact, the absorbed light energy may be changed partly into heat, partly into light of diminished energy or into any number of other forms of energy.

NATURE OF CHEMICAL CHANGES BROUGHT ABOUT BY LIGHT

Let us now consider what sort of chemical changes light brings about in passing through the earth's atmosphere. The answer to this question which especially interests the chemist is closely connected, as we may now assume, with the formation of organic from inorganic matter under the influence of light energy. The further step in the evolution of life from inorganic matter is the one which chiefly interests the biologist. It was first necessary for the earth to cool down to such an extent that the development of organic from inorganic matter might be possible. While we can only conjecture as to the temperature at which such development could have taken place, yet it is interesting to note the fact observed by the American scientist, Jacques Loeb, that in hot springs or geysers with a temperature of 55° C. no algae or other forms of life are present. Therefore, we can assume that the earth must have cooled to this temperature before a living cell could develop.

Logical considerations force the further supposition that the constitution of the atmosphere was different in the geologic

past from what it is to-day. The atmosphere was very rich in carbon dioxide and water vapor, and, in addition to the higher temperature just mentioned, it is probable that those of the sun's rays which are chemically active—namely, the violet and ultra-violet rays—must have been present to a far greater extent than they are to-day; it is a well-known fact that light sources of higher temperature radiate much more ultra-violet light than those of lower temperature.

We can, therefore, on the basis of modern research in physics, chemistry, and geology, get some conception of the conditions existing at that period in the earth's development, when inorganic matter was changed under the influence of light into living substances.

With the help of modern laboratory equipment we can imitate these conditions on a small scale and study the chemical changes which take place. It is unquestionably true that in the geologic past, as a result of violent volcanic eruptions, inorganic salts were largely present in the atmosphere, which doubtless were of great importance in the development of organic matter. For example, in recent volcanic disturbances strongly magnetic, complex salts of iron have been found which contain this metal linked in both the ferrous and ferric conditions. Salts of this constitution are particularly active as catalysts; they also possess the power of activating oxygen and of decomposing water molecules with the formation of hydrogen.

Effect upon Inorganic Matter

We shall now consider somewhat more exhaustively the chemical changes of the earth's atmosphere which are brought about by the influence of sunlight. It would be most desirable if we could begin by ascending in an aeroplane as high as possible and analyze chemically the air at this altitude. We shall compromise, however, by ascending the Swiss Alpine peak, Monte Rosa, on the pinnacle of which a small chemical laboratory, at an altitude of forty-six hundred meters, will simplify our chemical and analytical work.

Even on the way to this height, which leads over great glaciers, we notice on our skin the intensive action of the sunlight, and we must cover our faces with thick layers of vaseline to avoid dangerous sunburn. We wear dark glasses to protect our eyes against blindness from the brillance of the sun. The light of the sun which in the valleys has a beneficent and even healing effect becomes a dangerous enemy when we climb to the altitude of the glaciers. The reason for this lies in the fact that we are continually approaching nearer to the region of the ultra-violet rays of short wave length, which ultimately would destroy all life. Not only is the direct exposure of the unprotected skin to the light mortally dangerous, but in addition we are also likely to be slowly poisoned. The air which we breathe in the regions of perpetual ice lying around mountain peaks, such as Mt. Blanc or Monte Rosa, contains considerable quantities of poisonous substances, in particular nitric oxide, nitrous oxide, ozone, hydrogen peroxide, and ammonium nitrite, which change our blood and bring about severe illness. We believe that the so-called "mountain sickness" is partly a result of this kind of poisoning. From investigations which were carried out on the summit of Monte Rosa at an altitude of forty-six hundred meters, it appears that the gases, nitric oxide, nitrous oxide, and ammonium nitrite, which are found in this atmosphere, are decomposition products of a primary product which is extremely unstable and has the composition NOH. The compound NOH, which is called nitrosyl, is not less poisonous than prussic acid, judging by its great reactivity with aldehydes and with iron salts. Nitrosyl or its alkali salts have not yet been isolated in free condition, but we know from the important investigations of Angeli that there is a salt which contains sodium nitrosyl linked with sodium nitrite. With the help of this salt we can study the properties of the extremely unstable free acid called nitrosyl. It is a special peculiarity of those compounds occurring in nature which are particularly important in the evolution of matter, that as a result of their great reactivity it is impossible to isolate and identify them. To these compounds belongs nitrosyl, which it has been impossible heretofore to secure in the free state. In order to be able to identify such elusive compounds, we resort to a peculiar process, which is known in German as the "Abfangverfahren," and which consists in trapping or catching the desired compound by means of other substances which are added to the mixture, from which we expect to get the unstable product, and which react extremely easily with it.

The famous Italian chemist, Angeli, was the first to observe that nitrosyl reacts with aldehydes to form so-called hydroxamic acids, which can easily be isolated in the form of complex metal salts. The author and his collaborators used the method just described to separate the nitrosyl, which is formed from air and water by exposure to violet and ultra-violet light radiation—that is, formaldehyde was added to the mixture. The method proved to be practicable and they were able under suitable experimental conditions to isolate and identify the reaction product of nitrosyl plus formaldehyde—namely, formhydroxamic acid, $H-C\begin{matrix}\diagup NOH\\ \diagdown OH\end{matrix}$. Their method was confirmed by Baly except that this investigator, instead of using formaldehyde, passed carbon dioxide through an aqueous solution of potassium nitrate. Such solutions when exposed to mercury light form formhydroxamic acid, whereas they are entirely stable in the dark even after being subjected to heat. Finally, if simply an aqueous solution of carbon dioxide through which air is passed is exposed to radiation it is then not possible to isolate formhydroxamic acid, but by means of chemical reactions it can be proved that organic compounds containing nitrogen have been formed. By the union of nitrosyl with formaldehyde there is formed first of all nitroso methyl alcohol $\left(\begin{matrix}H\\H\end{matrix}\rangle C\begin{matrix}\langle NO\\ \langle OH\end{matrix}\right)$. As a logical consequence it can be assumed that nitroso methyl alcohol is the basic compound of the photochemical union of air, water, and carbon dioxide.

Nitroso methyl alcohol, which is sky blue in color, is an extremely unstable chemical compound, the existence of which can again only be shown by the aid of the above-mentioned "Abfangverfahren." Under ordinary conditions it almost immediately rearranges itself into formhydroxamic acid, or it decomposes with the formation of methyl alcohol and ammonia.

It is perhaps of general interest to learn that methyl alcohol is a good food for plants, which form from it sugar and starch, while ethyl alcohol acts as a poison to plants. For man and animals methyl alcohol is a strong poison, while ethyl alcohol in certain quantities is decomposed by the organism in metabolism without injury. Carbon dioxide dissolved in water can be changed by ultra-violet light of short wave length into formaldehyde, and in the presence of alkalies even into sugar—a fact which was first discovered by Stoklasa and later was confirmed and extended by Baly. A famous scientist once said humorously that in early geologic times it must have rained sugar water. By the formation of sugar from carbon dioxide, and the formation of nitroso methyl alcohol from potassium nitrate and carbon dioxide and water under the influence of radiant energy, we see that the problem of formation of organic from inorganic matter, under conditions such as obtained in nature, is solved.

Effect in Organic Processes

We shall now turn our attention to the question as to what organic compounds of a complicated nature can be formed from the basic substance nitroso methyl alcohol and its isomers by further action of light, and whether these compounds have any relation to the plant kingdom. When the famous Italian chem-

ist, Giacomo Ciamician, with whom the writer had the privilege of working, gave a lecture in this country entitled, "The Photochemistry of the Future," he emphasized particularly that we chemists must concern ourselves with the investigation of the secrets of the plants.

Green plants are clearly products of the light of the sun, and green leaves are the most wonderful photochemical laboratories in which those chemical compounds are produced upon which the whole life of man and animals is built. At the conclusion of Professor Ciamician's lecture, Professor Bancroft thanked him and said, among other things, "When I was young I was told to 'go to the ant thou sluggard,' but as I read it, the lesson of to-day is, 'go to the plant, thou chemist.'" This exhortation is just as timely to-day and in all likelihood it will still have great importance a thousand years hence.

Returning again to our reaction mixture formed from saltpeter and formaldehyde, we find in the mixture, besides nitroso methyl alcohol and formhydroxamic acid, a reduction product of these isomeric compounds—namely, formaldoxime, CH_2NOH—which because of its volatility can be isolated without difficulty from the other products. This compound must for many reasons be discussed in particular and described more exactly. You will certainly give this compound a great deal more attention when you know that it was found among the volatile substances of a cholera peptone culture, a fact which proves its importance in plant physiology. An aqueous solution of the substance is stable in the dark, but in light the molecule of formaldoxime rearranges itself to an extremely unstable compound which reacts with formaldehyde to form compounds of complicated structure. Besides prussic acid and methylamine there are formed nitrogen-containing rings, such as the pyrrole and pyridine rings, and also compounds which in their chemical properties are similar to the alkaloids occurring in plants. These compounds doubtless compare with those obtained recently by Baly and his co-workers by the exposure of ammoniacal formaldehyde solutions to mercury light. Among them will be mentioned in particular the alkaloid, coniine, 2-propyl piperidine.

The assumption that in those geologic times during which the earth was cooling slowly the atmosphere must have been filled with inorganic dust particles as a result of great volcanic eruptions, has been mentioned. These dust particles must have acted as promoters, or catalysts, in the photochemical processes which continually took place.

This train of thought led to the further study as light catalysts of such inorganic salts as can be found in present-day volcanic exhalations—for example, the strongly magnetic, complex ferro-ferric salt, which according to Werner's coördination theory has the formula $\left[\begin{matrix} +++ & CO_3 \\ Fe & (FeCO_3)_2 \end{matrix}\right]K$. It has been known for a long time that iron greatly accelerates many photochemical processes; this fact has recently been studied from an experimental standpoint by many different investigators, among them Fenton, McCallum, Dakin, and Neuberg. For example, tartaric acid is an entirely stable compound in sunlight; however, if an aqueous solution of this substance is treated with traces of an iron salt, such as ferric chloride, upon exposure to light an extremely rapid decomposition is produced. The mechanism of this peculiar action of iron remains unsolved.

When the author began his researches on the catalytic action of iron salts, the previously unknown fact was discovered that oxygen plays a vital role in iron catalysis. For through the union of iron ions or iron-complex ions with oxygen, the energy content of such ions increases, and they take on properties which approximate those of metallic iron. The role of oxygen in a few cases, such as in the action of ferrous hydroxide on potassium nitrate, is so striking that this process must be considered as a kind of inorganic fertilization. Ferrous hydroxide and potassium nitrate do not react at all, either cold or hot, in complete absence of air or oxygen. However, if air is admitted to the mixture it comes to life. The ferrous hydroxide molecule greedily absorbs a molecule of oxygen and is changed into an energy-laden, strongly magnetic ferrous hydroxide peroxide. This peroxide draws the alkali nitrate molecule into its field of affinity and reduces it to the nitrite—in other words, it splits off one atom of oxygen from the saltpeter. At the same instant that the nitrite is formed new reactions take place, which we cannot discuss here. The activated oxygen present in the reaction mixture at the same time acts as a strong oxidizing agent toward oxidizable substances which are present. For example, if an aqueous solution of saltpeter and methyl alcohol is shaken with ferrous hydroxide, then the air which enters brings about three different chemical reactions—namely, oxidation, reduction, and synthesis. The methyl alcohol is oxidized to formaldehyde, the nitrate is reduced to nitrosyl, NOH, and the two substances formed unite, with the formation of formhydroxamic acid. In this particular case the ferrous hydroxide peroxide assumes the role of light energy, since the same reaction is brought about by exposure to light in the absence of iron, as has previously been mentioned.

Besides iron, magnesium salts are also important light catalysts, but the function of these salts seems to be diametrically opposed to that of iron salts. While bivalent iron absorbs and activates oxygen and as a result of this property makes possible the respiration of living cells, magnesium has the power of activating hydrogen. This new assumption is based on the following experimental results.

If one exposes to sunlight an aqueous solution of magnesium nitrate containing formaldehyde, besides the organic compounds previously mentioned there are formed gases in considerable quantities. It is of interest to point out that the gas evolved on inoculating a bouillon culture with garden soil and the gas formed in the light reaction described above have nearly the same composition—i. e., both contain 50 to 80 per cent of nitrous oxide, besides nitrogen and traces of nitric oxide and prussic acid.

Many cases are known in which the same products that are produced by animal metabolism can be obtained by the action of light. This important fact is more easily understood if we consider that green plants build up from inorganic compounds—i. e., from air, water, and soil—with the aid of sunlight a great variety of products, such as sugar, starch, cellulose, protein, fats, alkaloids, pigments, rubber, etc., according to Nature's definite plan. The same evidence of natural law and economy is found in the way in which Nature brings about the breaking down of these substances in the animal kingdom. Thus, it happens that the same compound can be obtained on the one hand by photochemical decomposition, and on the other by life processes. This observation makes chemical researches with light still more interesting and important, and it proves at the same time that there is a close relationship between photochemistry and biochemistry.

If an aqueous solution of potassium nitrate containing formaldehyde and also a large quantity of magnesium carbonate is exposed to light, gas is formed which consists of 50 per cent nitrous oxide and 50 per cent hydrogen. The composition of this gas changes if magnesium nitrite is used instead of potassium nitrite, even working under exactly the same conditions. The gas formed in sunlight in this case contains no trace of hydrogen, but large quantities of nitrogen and small quantities of nitrous oxide are present. The initially formed hydrogen has been used up with the help of the complexly-bound magnesium in the subsequent exposure to light for the reduction of nitrous oxide to nitrogen. But hydrogen is actually formed first—a fact which can be proved by a shorter exposure of the mixture to light.

From the results obtained we can assume that magnesium salts under certain conditions are catalysts which stimulate light reactions and activate hydrogen. It is too early to establish any analogies between these results and carbon dioxide assimilation, in spite of Willstätter's investigations, which have proved that chlorophyll contains magnesium in complex linkage. We must always realize that only the intact cell, with its complicated colloidal structure, possesses the power of reducing carbonic acid, whereas the crushed cell is unable to bring about this change. It is hardly likely that this extremely important secret of nature will be revealed to us in the near future.

Our deeper conception of natural processes and their practical applications is obtained either from the instincts of primitive man or from the intuition of great geniuses. Thereupon, the scientist—for example, the physiologist or biologist—takes up the problem and investigates why and with what ultimate purpose Nature operates in the way she actually does. The chemist, however, studies matter from the standpoint of its molecular structure. If he can fathom this secret, then it is possible for him even to improve upon Nature.

A good example of this is the discovery of the action of suprarenine found in the suprarenal gland. Butchers have known for a long time that they could stop the bleeding of accidental wounds by applying the suprarenal glands of slaughtered animals to the wound. In modern times scientists who had a knowledge of this fact, especially biologists, were led to an investigation of the gland and its active secretion. Finally, the chemist took up the problem and investigated the molecular structure of the isolated active substance, and as a result of this knowledge he was able to synthesize from coal-tar products the pure substance adrenaline, or suprarenine, which is of great importance in pharmacology and surgery.

Importance of Photochemistry in Therapy

The three most important applications of light chemistry to therapy are: the exposure of healthy and diseased skin; the healing of tuberculosis, especially bone tuberculosis; and the healing and prevention of rickets in children. If we study folklore, we find it has always been known that people suffering from what was unquestionably bone tuberculosis were in the habit of exposing the diseased parts to sunlight in order to heal them. Also it was known that light and air were good for the prevention and healing of rickets.

It is very humiliating to think that science first realized the healing power of light after the discovery of artificial light sources, especially the mercury lamp. In the World War the blue light of the mercury arc was found even in hospitals very close to the trenches. At the present time when new hospitals are constructed special care is taken to facilitate the exposure of the patients to sunlight. Where circumstances and means permit, the hospitals are built on the southern slopes of mountains or hills, because the sun is strongest there. The physiologists, biologists, and physicians of the whole world are becoming more and more interested in light therapy. The chemist of a few years ago did not pay much attention to the chemical action of light, except in photography, and in this case only because of its practical interest. The layman in general thinks that photochemistry is the same thing as photography.

The chemist can also assist in the further study of light therapy by investigating the photochemistry of simple substances of biological importance, such as sugars or amino acids. From these results he may later be able to draw conclusions as to their relation to life processes. This path of research, leading to an investigation of the secrets of life, is indeed slow and arduous, but it has the great advantage that the investigator, just as the wanderer who climbs a mountain learns to know the way and looks back from the summit, sees familiar ground behind him.

In America the most important preliminary researches on the chemistry of tuberculosis have been made. In this connection may be mentioned those carried out under the direction of Levene, at Rockefeller Institute, on nucleic acids, which are constituents of cell nuclei, and further, the work of Johnson and Brown, at Yale University, with the tubercle bacilli themselves. We shall appreciate the importance of light in healing tuberculosis and be able to use it to greater advantage only if we discard empirical methods and carry out systematic investigations based on the chemical determination of the constitution of the tubercle bacillus. From a purely chemical standpoint we have at the present time, we regret to say, no idea of the direction in which to pursue a systematic study of the cure of tuberculosis with light.

In this connection we find a somewhat better situation in regard to researches on the prevention and cure of rickets and osteomalacia by means of light. Physicians and biologists have already found that ultra-violet light, which does not penetrate window glass, is especially active in the therapy of rickets. It is of the greatest interest that a daily exposure of three minutes to a mercury light at a distance of ninety centimeters suffices to prevent rickets in animals that would contract the disease in the dark or behind window glass because of a deficiency of calcium and phosphorus in their food.

Only a disturbance in the intermediate calcium metabolism can be considered as a cause of rickets or osteomalacia—i. e., rickets in adults. The reasons for the existence of such a disturbance are very complex and do not properly come under this discussion. What interests us, as chemists, is the fact that the relative and absolute quantities of calcium and phosphorus in the blood serum are in direct relation to the exposure to light. If the inorganic phosphorus content of the blood serum is decreased artificially by a diet deficient in phosphorus, it may be proved experimentally that ultra-violet light brings about an immediate increase in phosphorus content. These important investigations have for the most part been carried out in America.

What can the photochemist learn from these results? If the metabolism of calcium and phosphorus in the blood serum is so closely related to exposure to light, we must conclude, therefore, that perhaps they act as light catalysts. This assumption is supported by the close relation of calcium to magnesium, which, as previously stated, has the power of promoting photochemical reactions.

We see here again an instance of one science gaining from observations made in another and how we are led to new ideas and investigations. Only coöperation of scientists, or a mental symbiosis between physicians, biologists, and chemists, can lead to successful investigations of such difficult problems as the cure of tuberculosis or rickets by means of light.

In this day and age no man can be an authority on all subjects, and it is hardly possible for one man to be an authority on all branches of a single science. If the scientists of to-day wish to work for the universal benefit of mankind, they must follow the law of nature—division of labor. In other words, there must be the greatest degree of coöperation and teamwork.

Let us conclude with the words of the immortal Pasteur, which he once uttered to his sister and which may serve to characterize his career, "Life is valuable only in so far as it serves mankind."

Smoker

No meeting of the American Chemical Society is complete without a smoker, and for years one of the vexing problems of local committees has been to devise something so unique that the smoker will be remembered long afterward and taken as a standard of comparison. The New Haven Section undoubtedly spent considerable time and energy in preparing "Iono and Faradette," a chemical ballet which constituted the chief feature of the smoker held in the University Dining Hall Tuesday evening, April 3. A large orchestra furnished the music.

The Influence of Modern Chemistry on Pharmacology

By Arthur D. Hirschfelder

Department of Pharmacology, University of Minnesota, Minn.

There is a popular impression that the best physician is the man who gives the least medicine, and it is indeed true that the good physician of to-day prescribes fewer medicines than his grandfather did. His grandfather practiced according to the rule of tradition, with the general assumption that if a patient recovered it was the result of the treatment, but if he died it was in spite of the treatment. The modern physician uses only drugs whose effects have been thoroughly tried out on animals under perfectly controlled conditions, and uses them only to produce similar effects in man. But the modern physician has many more really useful drugs than were at the disposal of his grandfather and most of these have come to him through the influence of modern chemistry on pharmacology.

Arthur D. Hirschfelder

Most of our older drugs have come to us ready-made in plants, and the attention of pharmacologists was attracted to them because some savage used them as poisons or some old woman of folklore used them in a decoction to cure disease. It is true that the active principles have been extracted by ingenious chemical means, and that in the still newer and very useful remedies which have been extracted from the glands of the animal body—epinephrine or adrenaline, thyroxin, pituitrin, and insulin—still greater chemical skill has been exerted. These are worthy of still greater emphasis, because they have been given to the world by the chemists of America, and they represent perhaps the greatest triumphs of biological chemistry. However, in speaking to you as chemists in the few minutes at my disposal, I shall pass over the substances which nature has prepared for us in the plant cells and the animal body and shall confine myself entirely to the substances that are made in the laboratory.

A chemical substance becomes a drug when some one finds a use for it, and that can be done only after it has been tried out on animals or on the microbes or parasites of a disease. Still further, after this action has been tested in the laboratory, it must be tried out on hundreds of patients, before one can be sure that it has a better action than the drugs already in use for the same purpose, and that it has no unpleasant or detrimental actions which would preclude its use. And so among the hundreds of thousands of known chemicals, and the thousands that have been tried, hardly more than a hundred have found a permanent place in the daily practice of the modern physicians.

But it is these few which have been given us painless surgery, that have brought sleep to sleepless eyelids, that have lightened all manner of suffering, and, lastly and most important, that have led us to the paths along which we may march on to the cure of the infectious diseases.

It rarely happens that a useful medicine exists ready-made in the chemical laboratory, though occasionally a substance may be well known to chemistry for a generation before anyone tries it out and finds that it is well suited for use in practical medicine. For example, carbon tetrachloride had been well known for decades before anyone thought of trying it out as a cure for hookworm, and yet it has proved an excellent remedy. Benzyl alcohol and saligenin have proved useful local anesthetics, and numerous other common chemicals might be added to the list.

But most of our newer medicines, like our newer dyes, have been synthesized according to definite chemical principles—groups added by groups and tested out on animals, germs, and man, usually hundreds of compounds in the series before a practical result has been obtained. Indeed, the pharmacologist's problem is infinitely harder than the dyer's, because, though his drug, like the dyes, must affect one particular structure, the various tissues of the body which the drug must single out are much more nearly related chemically than are silk and wool. They are mixtures of proteins—that is, complex amino acids in colloidal form—dispersed or emulsified with fats and lipoids.

In order to understand the action of drugs, we may think of the body as built up of cells; each cell is something like a hen's egg, composed of three parts: the central part, the nucleus made up of phosphoproteins (nucleo proteins) where the oxidations seem to take place; the main body of the cell or the cytoplasm, which is apparently an emulsion of hydrated or water-soluble proteins, fats, and lipoids; and the outer surface layer, which some consider as a film of fats and lipoids, but which is more probably an emulsion with the water phase emulsified in fats and lipoids.

General Principles[1,*]

It will not be possible to epitomize all the contributions that chemistry has made to pharmacology. Therefore, I shall merely mention a few of the general principles which one must take into consideration for every organic substance, and then take up a few of the subjects which illustrate the progress that is being made.

We cannot proceed to the synthesis of new drugs unless we have some principles to guide us in our lines of thought, and so I shall devote a few moments to considering some of the general principles that influence the action of chemical substances in the body, which one must take into consideration with every new substance, and then proceed to illustrate how we have applied them in the study of a few groups of substances in which we have been especially interested.

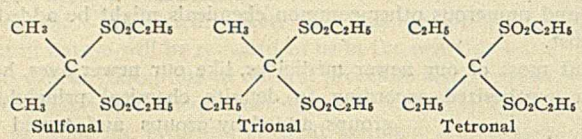
(1) The first real knowledge that a small change in chemical structure might cause a great change in the action of a drug came in 1859, when Stahlschmidt[2] showed that the mere addition of methyl iodide to the molecule of strychnine gave a substance which caused paralysis instead of convulsions; and in 1868, when Brown and Fraser[3] showed that this curare-like action was common to all quaternary ammonium bases, whether derived from the alkaloids or from other ammonium derivatives.

(2) The second great advance was made in 1854, when Bibra and Harless[4] and later in 1899 Overton[5] and Meyer[6] showed that all the general anesthetics are relatively inactive chemical compounds which are much more soluble in the ordinary organic solvents than in water. Meyer demonstrated that the soporific drugs of the sulfonal series ran exactly parallel to their coefficient

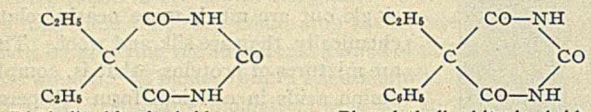
* Numbers refer to Bibliography at the end of article.

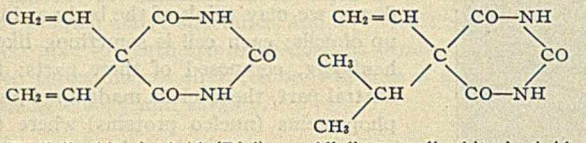
of distribution between lipoids and water. Trional with three ethyl groups is more lipoid-soluble and more potent than sulfonal with two, but tetronal with four ethyl groups is a less active soporific, and correspondingly its distribution coefficient between oil and blood serum is lower.

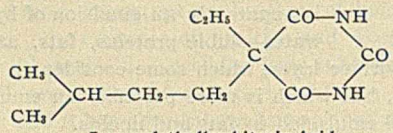
(3) Among these lipoid-soluble substances it usually appears that the longer the chains the greater the physiological action and the higher the toxicity, and often they seem to follow the rule that each additional CH_2 link in an aliphatic chain renders the substance three times as active and as toxic as the next lower homolog (Richardson,[7] Traube,[8] Kamm[9]).



(4) Naturally, therapeutic efficiency is determined by the so-called therapeutic coefficient, the ratio between the dose that just kills the animal and the dose that produces the desired therapeutic effect; and the substance with the highest ratio is usually the one that is most desirable. The newer soporific compounds, diallylbarbituric acid (dial-Ciba) and isoamylpropyl (Shonle and Moment[10]) and isoallylethylbarbituric acid (allonal) seem to be the most potent of all.







In order to understand this action we must remember that the cells of the body seem to be surrounded by a surface membrane of lipoids, upon which the substances must be absorbed or through which they must penetrate before they can act. Lillie,[11] Osterhout,[12] and McClendon[13] have shown that in low concentrations the anesthetics render the cell less permeable to ions, while in harmful concentrations the membrane becomes more permeable. Clowes[14] has found that the same relation applies to their effects upon the surface tension between oil and water. Low concentrations on the anesthetic increase the surface tension; higher concentrations decrease it.

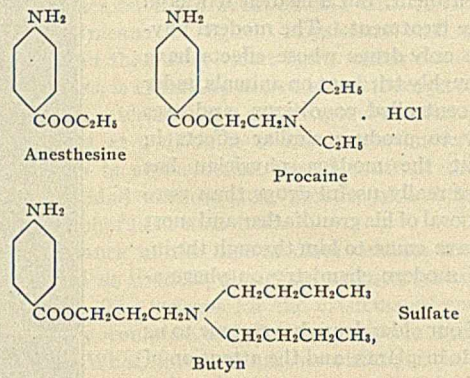
(5) Among the lipoid-soluble dyes, Ehrlich[15] showed that the basic dyes (NH_2 derivatives) stain the cells of the nervous system more frequently than do the acid (OH) dyes, and this need for basic compounds probably explains why so many of our medicines are nitrogen-containing bodies and NH_3 derivatives.

(6) Conversely, Salkowski and later Ehrlich demonstrated that when substances like phenol and the aniline dyes are rendered capable of forming water-soluble salts through the addition of carboxyl or sulfone groups, they are much less active upon the body and are more readily excreted through the kidneys, so that even the product formed by the sulforation of morphine no longer acts as narcotic.

(7) We must take into account, not merely the drug itself, but the subsequent changes which it may undergo within the animal body, and realize that its chief action may occur after this conversion has taken place. For example, Selling[16] showed that benzene destroys the bone marrow and the white blood corpuscles, whereas Winternitz, and Hirschfelder,[17] showed that toluene, which is easily oxidized to benzoic acid, has no such effect. Most of the esters are hydrolyzed within the body and exert their action through the products of their hydrolysis. Many of the amines, and especially the α-amino acids, are desamidized to the corresponding hydroxy acids, and are subsequently still further broken down by oxidation.[18] These are the general principles which seem to apply in almost all groups of substances.

From this point on we may say that the development of drugs has usually begun with some happy observation that a certain substance possessed a certain action and its derivatives have been prepared in accordance with these principles until the optimum of the series has been reached.

Thus, Einhorn[19] found that the esters of *p*-aminobenzoic acid exert a local anesthetic action on abraded surfaces, and gave us anesthesine, the simplest of this series. From this have been elaborated procaine, apothesine, and still more recently by Roger Adams, butyn, which, unlike all the others, can anesthetize the tongue and the mucous membranes of the mouth.[20]

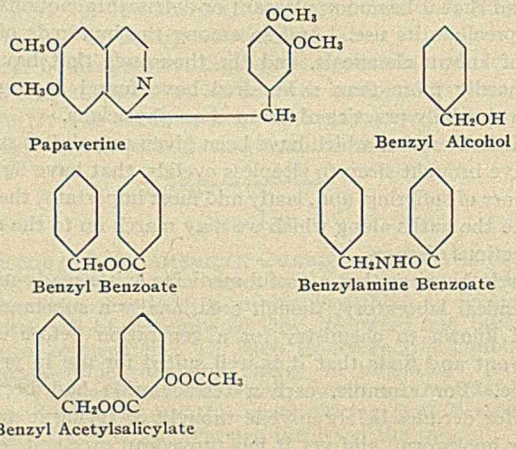


So much has been written upon the drugs that relieve pain that I am sure it is all familiar to most of you, and I shall therefore pass on to two subjects which have seemed to me important and interesting—the studies on the simple benzyl compounds to take the place of the alkaloids, and the chemical warfare that has been waged on the causes of the infectious diseases.

Alkaloid Substitutes

If we look closely at the structure of the alkaloids we shall see that most of them have three striking properties. They are tertiary or secondary ammonium bases, with pyridine, quinoline, isoquinoline, or phenanthrene rings, usually hydrated, and they are often either alcohols or the esters of alcohols.

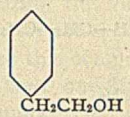
But their tremendous molecules unquestionably contain many groups which are unnecessary for their medicinal properties and which merely add to their toxicity. It was therefore a tremendous advance when Macht,[21] in 1918, demonstrated that papaverine owes its action to the benzyl portion of the group; and that benzyl alcohol is a definite local anesthetic and the benzyl esters cause relaxation of the hollow viscera in diseases which are brought about when these structures are in a state of contraction. Accordingly, he found that benzyl benzoate is useful in the treatment of many spastic conditions,



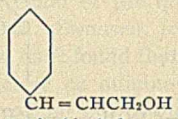
such as asthma, diarrhoeas, and especially painful menstruation. Litzenberg[22] found that it relieves about half of all cases of painful menstruation, but only those in which the trouble is due to an irritable uterus and not the cases where tumors or organic lesions are present.

Since then many other benzyl esters, the stearate, succinate, and phthalates[23] have come into use, and Volwiler[24] and Neilson[25] have shown that they act in proportion to their rapidity of hydrolysis. The most active of all is the benzyl ester of acetylsalicylic acid, but this is very peppery and must be used with caution on account of its irritating properties.

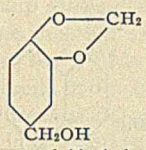
Since the alkaloids all contain nitrogen and the benzyl esters do not, it seemed interesting to find out what would be the effect of introducing a nitrogen group. Accordingly, we prepared benzylamine benzoate, in which an imine group replaces one oxygen. This compound is lipoid-soluble but very insoluble in water, and we have been surprised to find that we cannot produce relaxation of smooth muscle or any other noticeable physiological effect, even by painting an oil solution of the compound directly upon a contracted intestine. Following Macht's studies we have investigated other aromatic alcohols and found that of this series saligenin is the best and least irritating local anesthetic.[26]



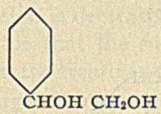
Phenylethyl Alcohol



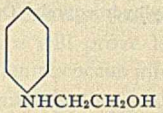
Cinnamic Alcohol



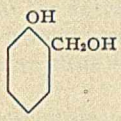
Piperonyl Alcohol



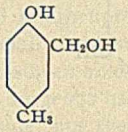
Phenyl Glycol



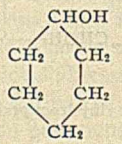
Hydroxyethyl Aniline



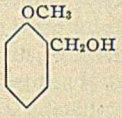
Saligenin



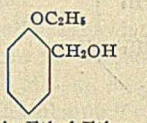
Homosaligenin



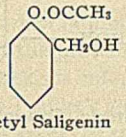
Cyclohexanol



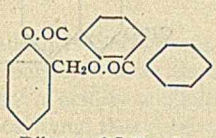
Saligenin Methyl Ether



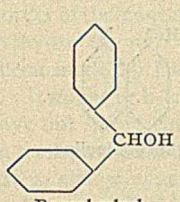
Saligenin Ethyl Ether



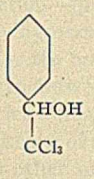
Acetyl Saligenin



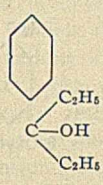
Dibenzoyl Saligenin



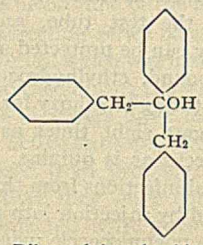
Benzohydrol



Trichlormethyl-phenylcarbinol



Diethylphenylcarbinol



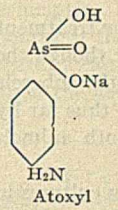
Dibenzylphenylcarbinol

Quigley and I[27] have studied a number of secondary and tertiary alcohols, such as benzhydrol, trichlormethylphenylcarbinol, cyclohexanol, diethylphenylcarbinol, and dibenzylphenylcarbinol, and found that the secondary alcohols are less potent locally than the primary anesthetics, and that the tertiary alcohols are apparently devoid of local anesthetic action. Hart, Jensen, and I[28,29] have studied the ethyl, butyl, isoamyl, and benzyl ethers of saligenin and the mono- and dibenzoyl and acetyl esters. Most of them possess some local anesthetic action and all of them relax smooth muscles beautifully in the animal, but they are all too peppery and irritant for clinical use.

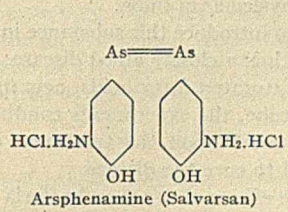
Chemical Warfare against Infectious Diseases

Unquestionably, the most important diseases that effect life and health are the infectious diseases; and therefore the chemical warfare upon the agents of these diseases is the chapter that seems to me to be of the greatest interest. And if that war is not yet won—if we have only penetrated the first-line trenches—the problem is all the more interesting and fascinating.

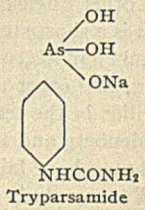
The conquest of syphilis by Ehrlich in the introduction of salvarsan (arsphenamine) is history that is well known to you all, for Ehrlich,[30] after studying 606 compounds in the transition from atoxyl to arsphenamine, along the chemical lines laid down in 1892 by his old collaborator, Michaelis,[31] who first described the group of twin-moleculed arsenobenzol compounds, has given us a real specific remedy for syphilis. After making over three hundred more compounds he introduced the water-soluble neosalvarsan. All these compounds, as shown by Bauer,[32] Meyers,[33] and Scherndal,[34] exist in toxic colloidal form, and Voegtlin[35] has demonstrated that their poisonous action is about proportional to their viscosity. While these researches were in progress Oliver and Yamada[36] showed that arsphenamine could be rendered much less toxic by the addition of a protective colloid like gelatin; and it is possible that this simple procedure may greatly diminish the number of bad reactions from the administration of this drug in practice. Voegtlin[37] has recently introduced a new compound, sulfarsenol, which is less irritating and can be injected under the skin instead of into the veins—a great improvement in administration. Jacobs and Heidelberger[38] have synthesized another arsenic compound, tryparsamide, with which Louise Pearce[39] has cured stubborn cases of the African sleeping sickness.



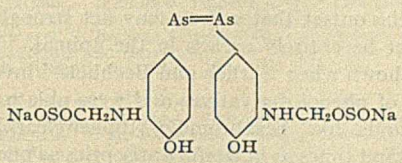
Atoxyl



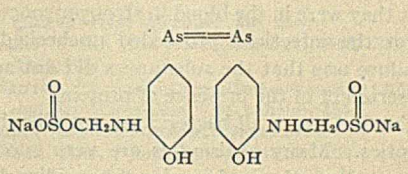
Arsphenamine (Salvarsan)



Tryparsamide



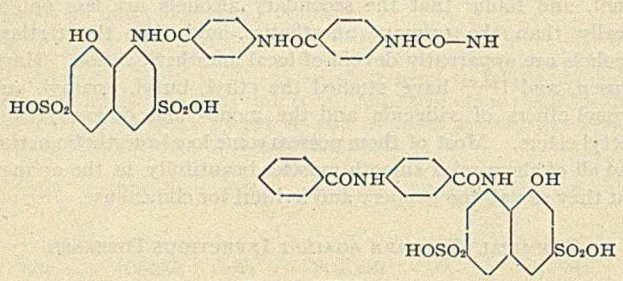
Neoarsphenamine



Sulfarsphenamine

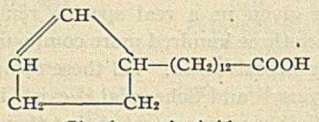
These compounds all contain arsenic, but almost twenty years ago Ehrlich and Shiga[40] demonstrated that a number of dyes,

especially those of the benzidine group, could be used for the treatment of experimental trypanosome diseases in animals. During the war, a new compound, "Baeyer 205,"[41] was developed, which



Baeyer "205"
(Probable Formula)

seems to be formed by a four-chained series of linked aminobenzoic acid groups, united at each end to an H acid. This compound seems to be specific for African sleeping sickness and other trypanosome diseases, and in the hands of English as well as German physicians has cured cases which have resisted all other treatments. It has shown two very interesting characteristics—less than one-hundredth part of the dangerous dose will cure the patient; on the other hand, the drug acts not by killing the parasite but merely by preventing it from multiplying in the body.



Chaulmoogric Acid

In the last few years Heiser[42] has added another triumph for the cure of a dreaded disease by curing leprosy with the injection of esters of chaulmoogra oil. This is the oil from a tropical nut. The esters of chaulmoogric and gynocardic acids are less irritating and are better suited to injection into the patient. These acids are long-chained acids with an unsaturated five-membered ring furthest from the carboxyl groups[43,44] (Power Walker). After ten months of treatment most early and moderately advanced cases can be cured and even advanced cases are often greatly benefited. Similar results have been obtained with the sodium soaps of these acids by Sir Leonard Rogers[45] and other English physicians in India.

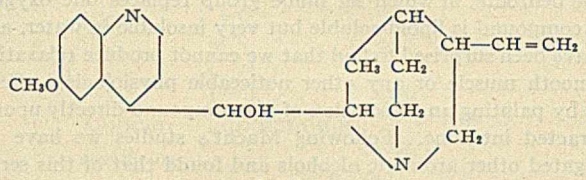
It is a short step to introduce this substance into the treatment of tuberculosis, which is a closely allied disease; but though the drug, like other unsaturated fatty acids, acts upon the tubercle bacillus in the test tube, the experiments conducted thus far by Lindenberg and Pestana[46] upon the treatment of both animals and man have failed to cure the disease.

We may study the effects of drugs on bacteria upon cultures in the test tube or by the treatment of infected animals or patients. We must realize at the outset that a drug may act strongly in the test tube and yet be entirely useless in the animal. This was most strikingly shown when Ehrlich and Bechhold[47] investigated a whole series of phenol derivatives and were able to obtain several compounds like hexabromdioxydiphenylcarbinol, which were two thousand times as powerful antiseptics as phenol. These substances could be safely injected into infected animals so that they were in the blood in stronger concentrations than this and yet the infections proceeded unchecked. The reason for this failure was that the substances did not act as antiseptics in blood serum or in the presence of proteins.

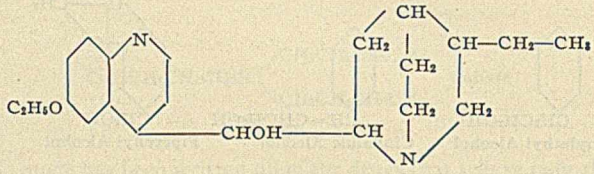
In the first place, all bacteria are not alike in their response to antiseptics. Many antiseptics are very specific. Thus, Lewis and Krauss[48] synthesized a series of benzidine derivatives, some of which were one thousand times as active against the typhoid bacillus as against the tubercle bacillus, and some, like resorcin, only ten to twenty times as active.

Churchman[49] has discovered that bacteria like the pneumococcus and the pus-forming cocci which take the Gram stain are more sensitive to basic dyes, and those which do not are relatively more sensitive to the acid dyes like acid fuchsin. This rule does not seem to be absolute, for we have found that pneumococci and streptococci are much more sensitive to the acid chitenin, an acid derived from quinine, and also to H acid, than is the Gram-negative colon bacillus.

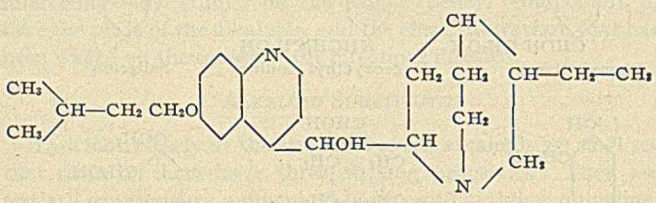
But the most interesting and most elusive of all the problems of medicine lies in the attack on the germs of pneumonia and the closely allied streptococci which are the cause of child-bed fever, rheumatism, heart disease, and the various forms of sinus disease and the pneumonia which follows influenza.



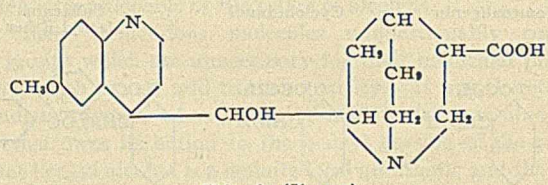
Quinine



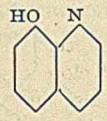
Ethylhydrocuprein (Optichin)



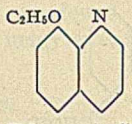
Isoamylhydrocuprein



Chitenin (Skraup)



8-Oxyquinoline



8-Ethoxyquinoline

The path was blazed in 1911, when Morgenroth,[50] showed that some quinine derivatives have a specific action against the pneumococcus in the test tube, and that if it is administered to mice they can be protected against infections from this germ. This compound, ethylhydrocuprein, is derived from hydroquinine by substituting an ethoxy for a methoxy group, and in the test tube is about eight times as strong an antiseptic against the pneumococcus as is quinine. It is equally specific in the treatment of local infections from this germ, like infections of the eye in man; and by injection into the spinal canal it has even been used to cure pneumococcic meninigitis in man, which

is usually fatal. Similarly, good results have also been reported in experimental empyemas caused by the same germ.

However, in lobar pneumonia it has proved disappointing. In 1912 I was unable to find any beneficial effects in thirty rabbits with experimental pneumonia; and Moore and Chesney[51] have similar experiences upon pneumonia patients. But the most disappointing feature of all is the fact that the drug is too poisonous for general internal use, and is liable to cause injury to the optic nerve, and even total blindness.

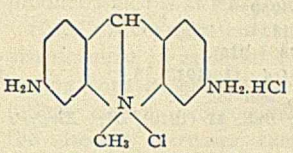
We have been anxious to see whether this specificity of the ethoxy group is confined to the quinine molecule, or whether it also exists in much simplex compounds. Accordingly, two years ago Pankow and I[52] studied the antiseptic action upon the pneumococcus of a series of ethoxy derivatives of simple aromatic substances, comparing them in each case with the corresponding hydroxy compound. In all these instances no difference whatever could be noted. Recently, Jensen and I have compared 8-ethoxyquinoline sulfate with 8-oxyquinoline sulfate, and here too we have found the results negative. Indeed, the oxyquinoline is a slightly better antiseptic than the ethoxyquinoline.

Since the simpler compounds seem to furnish us with no point of attack, we have also been studying the effects of modifications in the more complex ones. In 1879[53] Skraup showed that by oxidizing the vinyl side chain of the quinine molecule an acid chitenin could be obtained. Swansen, Jensen, and I[54] have prepared this compound and have found that chitenin hydrochloride is about one-fifth as active as quinine hydrochloride on the pneumococcus, and the sodium salt of the acid is practically devoid of antiseptic action. Fischer, in our laboratory, has shown that it is about one-fourth as toxic to rats, so that the antiseptic action is decreased less than the toxicity, and it would seem probable that the substance will prove less effective than quinine in the treatment of pneumococcus infections.

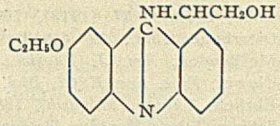
Morgenroth[55] has gone much further in the study of quinine derivatives. During the war he investigated whole series of homologous hydrocupreins, and found that the isoamyl and the octyl hydrocupreins possessed still higher antiseptic properties, especially against the streptococcus, so that with these compounds he has been able to cure local abscesses in animals; and the German surgeons used them during the war as antiseptics in surgical wounds; but they are too poisonous for internal administration. How far the specific action of these substances can be linked up with their physical properties is a fascinating but still open question.

Frey[56] has shown that when quinine is added to blood serum it increases the tendency of the proteins to coagulate under the influence of heat, and that this is independent of acidity or alkalinity. Eschbaum,[57] under Traube's guidance, found that the drugs of the hydrocuprein series lower the surface tension of water about in the order of their antiseptic action—quinine, ethylhydrocuprein, isoamylhydrocuprein, iso-octylhydrocuprein. Similar findings have been made by Larson[58] for the antiseptic actions of simple soaps. It might be interesting to draw still closer conclusions and to weave out interesting theories along these lines. But before we can transpose these into a theory of antiseptics, we must realize that in stalagmometer and other surface-tension phenomena we are dealing with the surface formed by air and water, and in antiseptics we are concerned with the interface between the blood plasma and the surface membrane of the bacteria.

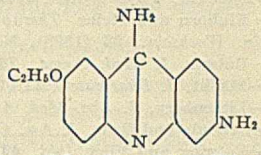
One of the most interesting series of antiseptic substances is the acridine or flavine series, which was first introduced by Ehrlich and Benda[59] and was studied during the war by Browning and his collaborators.[60] These observers have found that the acridine dyes are actually more active antiseptics in the presence of blood serum than in media free from proteins. Neufeld[61] and other observers have found that they have some value also for the treatment of animals infected with pneumococcus cholera and other bacteria.



Acriflavine (Trypaflavine)



2-Ethoxy-9-ethanolaminoacridine



2-Ethoxy-6,9-aminoacridine (Rivanol)

Morgenroth[62] has made a very interesting study of other acridine derivatives, applying to it the same methods as in the attack on the quinine derivatives. He has found that in the test tube 2-ethoxy-9-aminoethanolacridine, and especially the 2-allyloxy-9-aminoethanolacridine is extremely potent against pneumococcus and streptococcus, and that in the treatment of infected animals the ethoxy compound is good, but the allyl compound is useless. On the other hand, the 2-ethoxy-6-9-diaminoacridine (now marketed under the trade name "Rivanol") is very efficient, especially for the treatment of local streptococcus in animals and in man. In concentrations of one to two thousandths it does not irritate or injure the tissues, and, on the other hand, kills the cocci and sterilizes the wound.

One point which Morgenroth's studies illustrate, which American industrial chemists might well take to heart, is the fact that his studies were made possible through the coöperation of the manufacturing chemists. They made for him the substances with which he desired to work. It is only fair to say that it is impossible to get such coöperation in America at present. I do not like to, but in frankness I must, add that until such coöperation is possible we pharmacologists cannot compete with the Germans on even ground.

Conclusion

These represent a few of the studies which illustrate the influence of modern chemistry on pharmacology. The ground is broken and here and there a seed is sown. Further progress is certain, more certain wherever we can be guided by general principles, and especially by physicochemical principles, to point out the paths for syntheses. But whether or not chemotherapy can flourish on this side of the Atlantic depends entirely upon the coöperation of the chemists with the pharmacologists.

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(*Concluded on page 524*)

Cellulose Silk

By W. O. Mitscherling

Mt. Washington, Md.

CELLULOSE silk, or commonly called artificial silk, is not a substitute for natural silk, but is a product which must be placed in a class of its own. Many early attempts were made to prepare substitutes, but all that could be done was to imitate from Mother Nature a crude outline of the process.

Genuine silk consists of a coagulated fluid stream which emerges as a gummy liquid from two small orifices in the head of the silkworm and hardens in contact with air. The genuine filament contains as high as 18 to 25 per cent soluble gum, the sericin, and only 75 to 82 per cent represents the true silk, which is mostly fibroin. Only 300 to 700 yards of silk are reelable from each cocoon. The inner layers of the cocoons are so fine that it would not pay to reel them.

The mechanical part of Nature's process is to force a fluid through orifices into coagulating media. And this very part is adapted in the cellulose-silk industry. The fluids used are nitrocellulose, cuprammonium cellulose, viscose, and cellulose acetate. The coagulating media are air, water, acids, acid salts, and alkalies.

Cellulose Used for Silk

Before we can enter into a discussion of cellulose silks we must be familiarized with cellulose as a chemical compound. The fact that we are dealing with a highly complex compound prohibits the discussion of it in its molecular state in this address. And we merely have to compare forms of cellulose suitable for this industry with the purest form of cellulose as Nature presents it—the purified cotton, or normal cellulose. Chemical wood pulp always contains a small amount of lower carbohydrates, but with selective purification it is possible to isolate normal cellulose from wood pulp which is identical with cotton cellulose as a chemical compound.

Cotton cellulose must be purified before it can be used for cellulose silks; it must be freed from wax, oil and fat, pectoses, and mineral matter. This purification is effected by boiling with a weak caustic soda solution, and a subsequent bleach will remove coloring matter. The silk industry calls for high-grade linters, since there is no advantage in using long or medium staple cotton.

The average analysis of linters is about 89 to 90 per cent cellulose wood pulp; spruce contains as high as 40 to 52 per cent cellulose. Not all raw materials for the entire cellulose industry are produced in the United States. It is often thought that imported wood pulp is superior. However, the analysis reveals that American wood pulp as produced by the largest manufacturers actually turns out a product which is very superior to imported chemical pulp.

The structure of the cellulose molecule is still a matter which requires intensive investigation; however, very fine work has been done along these lines by Professor Hibbert.[1] His theory of an intramolecular glucosidic condensation of the dextrose molecule lends itself to the solution of a number of technical problems.

Both cotton linters and chemical wood pulp in their purified state are used for the production of cellulose silks. The type of process determines the source of raw material. So the nitrocellulose-silk process calls for linters. The same is true of acetate silk. The cuprammonium process adapts both linters and chemical wood pulp, while in the viscose process wood pulp is preferred. I do not wish to convey the idea that it is impossible to use linters in the viscose process; in fact, intensive experimental work is being done with purified linters for xanthates. But it seems that wood pulp dominates not only from the chemical, but also from the commercial standpoint. It seems further that certain impurities present in wood pulp check premature gelation and silk produced by the viscose process from linters is opalescent and takes up dyes unsatisfactorily. Very similar side reactions occur in the cuprammonium process, with the exception that cuprammonium silk produced from linters takes up dye remarkably well, but the softness of the filaments suffers. There is no doubt that in time our knowledge will bring forth differentiation in cotton and wood cellulose.

Nitrocellulose Process

The oldest method is the nitrocellulose process, or commonly called the Chardonnet process. Cellulose is nitrated to a proper degree—that is, it must be completely soluble in the solvent selected, which can be a mixture of ether and alcohol. The superfluous acid is removed by centrifuges and the nitrated product carefully washed. The excess wash water is removed again by hydro-extractors. The ester is dissolved either wet or previously

[1] This Journal, **13** (1921), 256.

dried, and forced through nozzles which are perforated with very fine holes to form filaments. This manipulation is termed "spinning."

Two spinning methods are in use by this process, wet and dry spinning. Naturally, the type of nitration differs with the type of process. In the dry-spinning process the filaments are set by air, and if the wet-spinning process is used the filaments pass through a setting bath, which may be water. The moisture of nitrated cellulose is gaged accordingly. To set nitrocellulose in air very rapidly, very wet nitrocellulose must be used. In the dry-spinning process the combinations of solvent ether-alcohol and nonsolvent water are so selected that the slightest evaporation of the lower boiler, ether, reaches a state in which the nitrated cotton is insoluble and therefore coagulation takes place. The evaporation is accelerated by heating units. The solvents are naturally recovered as much as possible. In the wet process, on the contrary, the solvent is diluted with a nonsolvent during the process of spinning, and coagulation of the threads takes place by passing the nitrocellulose solution through a water bath. The water content of the nitrated cotton can be therefore considerably lower.

In both cases the filaments are collected on spools or drums, subjected to further extraction of the solvent, and finally partially dried under tension. The filaments are collected in bunches of 12, 18, 22, 36, and even 72, to form a thread. This thread is highly inflammable and must be subjected to a process which removes the nitro groups, leaving cellulose, or, in other words, is denitrated. This is accomplished by immersing the silk into a solution of alkaline sulfide.

After denitration the silk is again washed and subsequently bleached. It is then reeled and twisted so that each yard of silk has about 100 twist, and is skeined into 2500- to 3000-yard skeins, in which state it is marketed.

Cuprammonium Process

The cuprammonium-cellulose process (Despaisses and Tauly process) is based on the property of cellulose to dissolve in copper hydroxide and ammonia. This may be accomplished by several methods. One, older, method is to treat copper turnings with ammonia, preferably in the presence of lactic acid. This cuprammonium solution dissolves pure cellulose rather slowly, but reacts very fast when the cellulose is previously mercerized. A later improvement is to mix the cellulose with copper hydroxide paste and dissolve this mixture in ammonia; or, vice versa, the cellulose is soaked in ammonia and copper hydroxide paste is added. A very stable copper-ammonium-cellulose solution can be obtained by this process.

The devices for thread formation are very similar in all processes. Spinning apparatus of various types are used, but in principle the cellulose solution is forced through nozzles with very fine holes, which are called spinnerets. Spinnerets are made of platinum, noncorrosive alloys, or glass.

The setting bath for the cuprammonium process consists of sulfuric acid alone, or the collected filaments are first set in an alkaline bath and the copper salts removed afterwards with sulfuric acid. The salts formed are soluble in water and washed out with water. The silk is treated by similar methods, as in all silk processes to produce soft filaments resembling the genuine article.

Viscose Process

The most popular process is the viscose process (Stern). Cellulose is first mercerized without removing the caustic soda, and the mercerized product is treated with carbon disulfide to form the cellulose xanthate, which is dissolved in water. The cellulose solution is matured and put through the spinning operation by pressing it through very fine holes into a setting bath, which is an acid or an acid-salt solution. The sulfur compounds formed are removed by alkaline solutions and the filaments carefully washed, dried, and put through various processes to produce a product which is at least equal to other cellulose silks.

Since viscose solutions undergo a progressive decomposition viscose must be spun at a certain stage of maturity, and the setting bath is selected accordingly. Viscosities of viscose solutions change progressively with the decomposition. First, the viscosity increases, then gelation takes place, and finally the cellulose separates out in form of a translucent cake. It is possible to produce viscose threads with great fineness.

Cellulose Acetate Process

The cellulose acetate process (Donnersmarck) consists in acetylating cellulose with a mixture of glacial acetic acid and acetic anhydride in the presence of a catalyst, which may be sulfuric acid or a zinc salt. The acetate is dissolved either in acetic acid or another solvent, such as ethyl acetate, and discharged through orifices into a nonsolvent, such as water, to form a thread.

It is claimed that acetate silks are but little affected by moisture. Acetate silks are just as soft in touch as other cellulose silk. Acetate-silk possesses great resistance to moisture and dyestuffs. It is further distinguished by its low density in comparison with other cellulose silks.

Present Problems in the Industry

All processes require skill and experience, and while the statement has often been made that most difficulties are mechanical, it must be remembered that those mechanical difficulties have been, and can be, satisfactorily eliminated only by chemists with mechanical ability.

Concentrations and viscosities are most important factors. It must also be remembered that cellulose silks are produced by a multistep process, and that, finally, the cellulose must be regenerated as such, but in form of a thread with sufficient strength, tenacity, and durability.

The conversion of cellulose into a compound which is soluble in some solvent and the regeneration of the same cellulose in its purest state with physical properties resembling genuine silk requires not only knowledge of the compound cellulose, which can be acquired only by patient and intensive research, but also a study of practical mechanical research.

For the past decade Europe could draw on cheap and efficient labor. Father, son, and grandson worked in the same plant, even in the same plant department. Their skill and efficiency were so highly developed that there was no necessity for automatic devices and combination of two or more chemical steps. To-day we work with an independent class of labor, a labor body which changes permanently, and therefore the cost of production increases automatically. New kinds of apparatus are devised which have almost revolutionized the cellulose-silk industry. And again, it was America who took the leadership in centrifugal spinning on a commercial scale.

Many plants are still operating by collecting the untwisted filaments onto spools or drums. Without any question, this method produces a high-grade silk, but it is wasteful. The latest improvements are to twist while spinning. Centrifugal spinners, therefore, replace the older method, but with this replacement new factors enter the field. The process must be better controlled, and the composition of cellulose solutions and setting bath changed. More research, mechanical ingenuity, and tremendous initial cost of installation and upkeep of plant are required.

The scope of the cellulose-silk industry can be seen by the quantities used. In 1922 about 23,000,000 lbs. of cellulose silk were produced. This is about 3 per cent more than genuine silk. It is true that cellulose silk will never replace the genuine silk, but, at the same time, the textile industry realizes that this relatively new fiber gains importance every day. It produces not only the most beautiful textures, but it lends itself to limitless possibilities. Regardless by which process the cellulose silk is produced, each has a splendid market of its own.

The Dedication of Sterling Chemistry Laboratory

Presentation of the Keys

By George H. Church

Representing the Sterling Trustees

As one of the trustees under the will of the late Mr. John W. Sterling, I have the honor of acting on their behalf in the dedication of this building, constructed and equipped with funds furnished from Mr. Sterling's estate and named in his honor "Sterling Chemistry Laboratory."

Those of you who were personally acquainted with Mr. Sterling will recall his many admirable qualities. I may be permitted to refer to a few of the leading events in his active and busy career. He was graduated from Yale in 1864, valedictorian of his class and a Townsend Prize winner. He took a post-graduate course, principally under Professor, afterwards President, Porter, and received his LL.B. degree from Columbia Law School in 1867. In 1893 Yale conferred upon him the honorary degree of LL.D.

Soon after beginning the practice of law in New York City, Mr. Sterling became a partner of the late David Dudley Field and Thomas G. Shearman, composing the firm of Field & Shearman. Upon the retirement of Mr. Field, in 1873, the firm of Shearman & Sterling was formed; and although Mr. Shearman died in 1900, the firm name was continued by Mr. Sterling, and since his death it has been continued by Mr. John A. Garver, Yale 1875, who for many years was a partner with them.

For more than thirty years prior to his death I was closely associated with Mr. Sterling and his firm in the conduct of their trust and other matters of an accounting nature, and I was in a position to observe the single-mindedness with which he applied his untiring energy, his business sagacity, and his great experience to the interests of his clients. His foremost thought in connection with every matter committed to his care or with which he had any association was service, the best service that he could render with the assistance that was available to him. He gained easily and completely the absolute confidence and trust of all who came in contact with him, no matter how exalted or how humble.

There were two objects to which he was especially devoted: the Miriam Osborn Memorial Home and Yale University. The Home was established under the will of Mrs. Miriam A. Osborn, widow of Charles J. Osborn, who in her lifetime (doubtless at the suggestion of Mr. Sterling) donated Osborn Hall to Yale, in memory of her husband, and also provided funds with which the biological laboratory was subsequently built. Mr. Sterling was the active executor of Mrs. Osborn's estate, and devoted much time and attention to the establishment and operation of the Home at Harrison, New York, for the benefit of needy gentlewomen who may there pass the remaining years of their lives among comfortable and attractive surroundings; and he personally added very largely to the generous fund provided by Mrs. Osborn. But Mr. Sterling's main objective and the inspiring incentive of a lifetime was his Alma Mater. That steady devotion never faltered. He never married and the wills which he made at various times always left the great bulk of his fortune to Yale, for the erection and maintenance of buildings and the creation of professorships and scholarships. Already ten professorships have been endowed, this building has been completed, the Sterling Hall of Medicine is now in course of erection, and a library building is contemplated, which it is hoped to make the crowning achievement of Mr. Sterling's benefactions and the enduring testimonial to his love for Yale.

Therefore, in partial execution of this great trust, I now, on behalf of Mr. Sterling's trustees and in his name, present this chemistry laboratory to Yale University, assured of the great benefit that it will prove to this and succeeding generations.

Acceptance for the University

By President James Rowland Angell

ON BEHALF of Yale University, I gratefully accept this superb monument to the love and devotion which John W. Sterling bore his Alma Mater. On this spot generation after generation of eager youth will be taught to recognize, obey, and direct to man's needs the fundamental laws of nature. Here the ablest minds will delve continually into Nature's secrets, unlocking her treasures for the increasing happiness of all mankind. Industry and art, agriculture and commerce, medicine and engineering will be the constant beneficiaries of the labor here expended. And perhaps best of all will be the ever more penetrating insight into the marvelous composition of the great universe in which we live.

In every contribution which is here made to learning and to human welfare, Mr. Sterling will have a share, and to him and to you, Sir, the representative of his faithful trustees, under whose careful guidance this great gift has been administered, we record our enduring gratitude.

It seems fitting on this occasion to call to mind, however briefly, a few of the men to whom the University is most conspicuously indebted for the development of chemistry. The history of this science at Yale began 119 years ago to-day when Benjamin Silliman, responding to an invitation of President Dwight, gave on April 4, 1804, his first lecture on chemistry in a building since destroyed, which stood on the south side of Chapel Street. In 1853 he became professor-emeritus, and in the intervening period not only established firmly the interests of chemistry as a subject of academic instruction, but also in 1818 founded the *American Journal of Science*, which is still conducted by his grandson, Prof. Edward S. Dana. He furthermore succeeded at an early date in gaining academic recognition for mineralogy and geology and was actively instrumental in the founding of the Sheffield Scientific School.

Among his students and assistants were his son Benjamin Silliman, Jr., who subsequently succeeded to the professorship of general and applied chemistry, John P. Norton, later professor of agricultural chemistry in the Sheffield Scientific School, Prof. George F. Barker, afterward at the University of Pennsylvania, and Oliver T. Hubbard, subsequently professor at Dartmouth College

In 1856 Samuel W. Johnson was appointed professor of analytical and agricultural chemistry and served for forty years. Through his efforts the Connecticut State Agricultural Experiment Station, of which he was made director, was established in 1877, and, this being the first institution of its character, he thus became the founder of the great movement which has since spread all over the country affecting the national practice of agriculture in the most fundamental way. Not only through his own contributions, but through the training of a remarkable group of distinguished students, among whom mention may be made of Chittenden, Jenkins, Atwater, Armsby, and Osborne, he left enduring contributions to agricultural and physiological chemistry.

Few men in American science have achieved a more eminent position than J. Willard Gibbs, who was professor for thirty-two years in Yale, having been appointed professor of mathematical physics in 1871. His fundamental contribution to the formulation of the principle of chemical equilibrium is recognized to-day as one of the great outstanding achievements of modern chemical theory.

The continuing work of Russell H. Chittenden is so fresh in the minds of all who are here gathered that it is needless to enlarge upon it, but it is simple justice to say that physiological chemistry in the United States owes more to him than to any other one man, and he has shown himself a worthy successor of the great group of chemists who have preceded him at Yale.

There are many other men whose names might well be added to this list of contributors to the development of chemistry in the University, but we must content ourselves with these few instances.

It is surely appropriate that we should on this occasion recognize also those who have provided the buildings and the resources wherewith our chemists have done their work. In the early years chemistry led a nomadic existence, having apparently been originally conducted by Professor Silliman in

a kind of dug-out in one of the old college buildings, and afterward the basement of the president's house appears to have been devoted to the advanced work in this somewhat submerged subject. Later, use was made of the old Commons building.

Shortly after the establishment of the Sheffield Scientific School, a considerable part of the chemical work was moved into the old medical building, now the headquarters for the administration of the Sheffield Scientific School, and in 1895 there was completed the Sheffield Chemical Laboratory, built by the contributions of several donors. In 1886 Albert E. Kent, of the class of 1853, appreciating the fundamental significance of chemistry for the modern world and desiring that the students of Yale College enjoy to the full the benefits of contact with this great field of knowledge, erected the commodious building, which bears his name, at the corner of Library and High Streets, where, until the present year, the chemical work of Yale College has been carried forward. In 1901–2 he made an additional contribution and in 1906 his son, William Kent, of the class of 1887, responding to the needs for additional space, generously gave the necessary funds for improvements and for the adding of another floor to this building, thus completing the original plan. Prof. Frank A. Gooch had been appointed in 1885 to have charge of the college department of chemistry.

The remarkable increase of interest in chemistry and the greatly augmented number of students, not only undergraduates, but graduates and members of the professional schools desiring to pursue chemical studies, led to the request of the corporation to the trustees of the estate of John W. Sterling to consider the erection of a university laboratory of chemistry, and the great building in which we are now gathered is the outcome of this request. May those who labor in it be worthy of the great ideals which animated the founders of their science, and of the noble men who have preceded them in its development here at Yale!

To the A. C. S.

And now, Dr. Franklin, it is my privilege and pleasure to turn over to you as President of the American Chemical Society the use of this beautiful structure for your purposes during the week we are so fortunate as to have you with us. The University puts itself at your disposal and trusts that you may find agreeable the various arrangements provided for your convenience.

[President E. C. Franklin, responding for the Society, expressed the gratitude of that body for the University's hospitality, and accepted the laboratory for use during the meeting.]

The History of Chemistry in America, with Special Reference to Yale

By Edgar Fahs Smith

University of Pennsylvania, Philadelphia, Pa.

I AM INDEED grateful for the opportunity of speaking to you on the history of chemistry in America, with reference to Yale. This is an epochal occasion, and while we rejoice in the possession of this magnificent, palatial edifice, designed for the service of chemistry, it is well, in this moment of exultation, to take a backward look and note the "rock from whence we were hewed and the hole of the pit from whence we were digged." So, with your permission, I shall briefly touch upon facts "pick'd from the worm holes of long vanish'd days and from the dust of old oblivion rak'd."

Chemists—American chemists—in tracing the history of their science, are apt to turn to other countries. For chemistry was born in the dawn of civilization and to older lands one looks for its gradual evolution. As the oldest of the experimental sciences it is coëxistent with man's own rise and development. One need not search far to find evidences of its presence. Yet, Americans have frankly admitted their ignorance of the earliest days of chemistry in this western world. In fact, it has been only within the last quarter of a century that any effort has been put forth to ascertain when chemistry had its beginnings among us and what contributions it has made to the upbuilding of society.

The Beginnings in this Country

It is to Jamestown, Virginia, founded in 1607, that the student of the history of chemistry must go, for there in the year 1608, before the "ring of the axe was heard in the forests of America," bold spirits erected a glass house "in the woods," producing a product which was sent home, in crude form, but still proof of the possibilities of an industry which might contribute to the maintenance of the settlement and to the coffers of the mother land. Glass beads made in that glass house exist to-day, showing that this product of chemical activity had for its purpose a means of effecting trade with the aborigines, who were attracted by the pearly-colored objects. And in 1619 two or three furnaces for the reduction of iron ores were in operation not far away.

Chemistry was rapidly serving man in this then distant land at a day less than a century and a quarter after its discovery by the immortal Columbus. What more might have been accomplished in addition to the extraction of coloring matter from new plants, in addition to the isolation of substances possessing medicinal virtue, can only be conjectured, for further attempts were frustrated by the frightful, appalling massacres perpetrated by the Indians in 1622. The glass house and furnaces were completely demolished. Dead was chemistry in its applications at Jamestown.

To the Old Bay State the student must next go. For there it was that John Winthrop the younger, a graduate of Dublin, an early member of the Royal Society, inaugurated chemical work by the development of ore industries, which he carried far along in the State of Connecticut, of which he became the first governor. He held frequent correspondence with scientific friends in London. At their suggestion, and following, too, his own thought, he experimented widely, bringing to light many highly interesting facts, afterwards placed upon the pages of the *Proceedings of the Royal Society*. As an associate of the leading alchemists of England, as a believer and promoter of the art of transmutation of the baser into the nobler metals, he breathed into the atmosphere about him the spirit of the projector or alchemist; and traces of that spirit continued far into the eighteenth century, subtly enchaining a son of Yale, born in New Haven, a minister of the Gospel, a lawyer, and again a preacher of the Word, and finally, seventh president of Yale—Ezra Stiles.

Yale's First Promoter of Chemistry

It is he who must be regarded as Yale's first promoter of chemistry. In existing records it is noted, among other things, that Stiles repeated Priestley's experiments on fixed air; that he impregnated water with it, thereby making artificial "spa water;" and that in his leisure moments, generally at night, he tried certain reagents, and wrote, "If spirits of sea salt or the muriatic acid be drawn over the semimetal called manganese,

it becomes a solvent of gold." This fact had been mentioned by a Mr. Jones, who delivered a chemical lecture in New Haven. And from this same Mr. Jones, Stiles had received a quantity of vitriolic ether which apparently engaged his study for quite a little while. He observed that "the æther imbibed a solution of gold and the next day when commixt with the aqua regia was again separated and held the gold distinctly separated."

All this while Stiles was reading Macquer's Chemistry, from which he made a selection of experiments, performing them with more or less success, always at night. He was truly an enthusiastic student of chemistry. Men who had had experience in the science visited him, and together they held discourses on chemistry and made inquiry concerning the hermetic philosophy. Stiles was in ecstasies when Dr. Eneas Munson, of New Haven, showed him a piece of malleable, whitish metal, "which he himself made within a month past. It was fixed mercury, the first I ever saw," said Stiles.

One gathers from the notes of Ezra Stiles that in addition to his many duties as president of and professor in Yale, his fondness for chemistry led him to speak of it and of the remarkable discoveries, unfolded through its agency, to his classes. He corresponded with Franklin, whom he idolized, and to him he gave account of his practical work in the science. Self-trained, it is but natural that he should have presented his subject in a crude form. There is also no question but that the matter of projection or transmutation was in his mind. He endeavored to free himself from it, with but partial success, for he was the intimate of Dr. Munson, Judge Danforth, and the Reverend Mr. West, of whom he said, "They believed in the reality of the Philosopher's Stone, although neither of them ever obtained it." And in his diary occur these words, "Terra Fol, aethere sublatâ hodie." Absolute proof that he was really dabbling in alchemy! And yet, perhaps because in the thought of most people alchemy, the black art, belonged with witchcraft, Ezra Stiles did not care to be allied with those who practiced the latter. He was perturbed; and, a little suspicious of himself, exclaimed:

> I am not versed in the books of the adepts. I have seen but a few of these authors and read less. Perhaps all the little I have read collectively would not equal a common octavo volume. I am infinitely less acquainted with them than any other of the sciences in the whole encyclopædia. I have never observed the Extracted Sulphur of Gold in Terra. I have no practical knowledge of the matter: the few ideas I have about it are only imaginary, conjectural, and speculative. Coram Deo Veritas.

Dear old Dr. Ezra Stiles! We rejoice that you turned from witchcraft, which looks backward, but are profoundly thankful that you were, despite your lovely disclaimers, allied with alchemy, which looks forward; for truly it was experimental science in the making, a science that does not yet acknowledge its finite bounds, but aspires, star-eyed, to illimitable possibilities. Yes, you were Yale's first experimenter in the science which has called us together this morning, and may your benign, fatherly spirit at this moment rest approvingly upon all who are here, rejoicing with Yale in this new abode of chemistry.

Silliman the Elder

Time rolled on. The soul of Ezra Stiles went out on the lonesome trail, and another son of Yale who, like Stiles, became a lawyer, but animated by the latent purpose of the dear old alchemist in his predilection for chemistry, heeded the call of Alma Mater, in 1802, to the chair of chemistry. Before assuming its duties, however, he journeyed to Philadelphia, then the center of art, literature, and science, that he might sit at the feet of James Woodhouse, the Napoleon of experimental endeavors in America. Let us, for a few moments, follow this eager, earnest student—Benjamin Silliman, the elder.

What a delightful company awaited him in his lodging house in the City of Brotherly Love: Horace Binney, Charles and Elihu Chauncey, and Robert Hare—young men of great prominence—educated men—men of elevated position in society, their manners in harmony with their training. Silliman wrote:

> As Robert Hare was a brewer of porter and was one of our number, his porter was in high request, and indeed it was of an excellent quality. He was a genial, kindhearted person, a year younger than myself, and a proficient in chemistry upon the scale of that period. Hare invited me to join in the study of his oxyhydrogen blowpipe.

While perceiving that this instrument was ingenious, Silliman saw that it was unsafe as regards the storage of gases, and its correction in this particular was entirely due to him.

It was a genuine pleasure for Silliman to stand by his friend Hare in 1802, when Hare repeated his blowpipe experiments before Dr. Joseph Priestley, James Woodhouse, Thomas Cooper, Adam Seybert, and others. One wishes that he might have a picture of that group!

The possibilities of the oxyhydrogen flame were constantly in the thought of Silliman, and the very first pneumatic trough, including Hare's blowpipe, was constructed by Silliman for the laboratory of Yale College in 1803. In later years he wrote:

> The fusion and combustion and complete dissipation of platinum, gold, silver, nickel, cobalt and most of the metals, and the fusion of the principal earths and of their more refractory compounds have been made familiar and easy class experiments of every course of chemistry in Yale College for years.

Silliman and Hare were pupils of Woodhouse, who, when interrogated upon the brevity of his didactic lectures, replied, "that no man could dwell, in discussion, on a single topic more than five minutes without talking nonsense."

They were acquainted with his laboratory and the remarkable experimental work conducted by him, but in their leisure hours did very independent thinking and experimenting in their own laboratory in the basement of their lodging house.

To them it was delightful and profitable to meet Dr. Priestley very frequently at the home of Wistar. As Silliman was taking a broad view of science and its teachings, his hours with Wistar the anatomist, Barton the botanist, and Seybert the mineralogist were precious. In his mind were revolving brilliant schemes for the elaboration of all these subjects, side by side with his thoughts on chemical research.

His friendship with Hare was unique. From their correspondence, continuing through life, it may be inferred that they were believers in and real promoters of genuine experimental science. They discussed its possibilities to and fro, and mutually submitted plans for the elucidation of the chemical and physical problems which interested them. While their active co-experimentation ceased upon Silliman's return to Yale in 1804, they wrote many letters regarding their common love—chemistry.

Silliman began his teaching career in a subterranean lecture room fitted up for his laboratory, which was fifteen or sixteen feet below the surface of the ground. It was inconvenient, it was so gloomy—but there he courageously worked for fifteen years. There he analyzed minerals and meteorites, and invented and perfected apparatus for demonstration purposes in chemistry and physics. In 1805 he was off again, this time to Europe, meeting in London Frederic Accum and Humphry Davy; and in Edinburgh John Murray and Thomas Charles Hope, the polished, stately, and formal gentleman who succeeded the gifted Joseph Black. In Edinburgh Silliman fairly reveled in the teachings of the Wernerian and Huttonian geological schools. He grasped the prevalent geological thought. But in 1806 he returned to New Haven, his days of tutelage passed and his actual teaching career begun. Mineralogy, geology, and pharmacy were added to chemistry. He proved a most inspiring teacher, and founded in 1818 that splendid medium of circulating the scientific work of his colleagues and himself—the *American Journal of Science*, now in its 105th year. And further,

he was prominent in the establishment of many Yale activities, flourishing at this moment—the Art Gallery, the Astronomical Observatory, the Medical School, and the Sheffield School of Science.

But to look once more upon Silliman as a research chemist. His *fidus Achates*, Robert Hare, had devised an unusual battery—a plunge battery of powers not before suspected. Hare transmitted all his experiences with this instrument to Silliman, and even sent him a well-constructed "deflagrator," as it was termed. Both experimenters marveled at the occurrences on attaching carbon rods to the deflagrator and studying the arc which ensued. In March, 1823, just one hundred years ago, Silliman wrote Hare:

> I gave you . . . . . an account of the fusion and volatilization of carbon by the use of your Galvanic Deflagrator. I have now to add, that the fusion of plumbago (black lead) was accomplished yesterday by the same instrument.

Again Silliman sought to ascertain the behavior of diamonds in the oxyhydrogen flame, and said, "They exhibited marks of *incipient fusion*." And thus it continued. Should the thought enter the mind of any one that Silliman was not a producer in his favorite science, let him read the voluminous correspondence which passed between him and Robert Hare. He will then promptly assign him a high place among researchers. The story of his laboratory would make a good prelude to the history of university education in this country as distinguished from collegiate.

Silliman possessed the genuine instinct of discovery, the quick recognition of new and interesting facts, and enthusiasm in following them up to novel and important results. That his successes in other directions somewhat overshadowed them does not detract from their permanent value, "for it must not be forgotten that those who smooth the road to science, and facilitate its acquisition to others, are often more permanently useful than such as are supereminently learned themselves: the greatest personal or mental acquirements die with the possessor; but those who labor that others may be wise, are a benefit to all posterity." (Mavor)

Is it not to the inspirational teaching of Silliman that American science is indebted for Dana, world-renowned geologist and mineralogist; Brush, whose exhaustive mineralogical chemical studies are authoritative everywhere; Johnson, pioneer leader in chemistry applied to agriculture; Willard Gibbs, first among physical chemists of modern times; T. Sterry Hunt, profound in chemical philosophy and theory; and hosts of others—giants in the world of natural and physical science?

Last evening I stood "under the friendly silence of the moon" before the bronze figure of Benjamin Silliman, out on yonder campus; how I wished that I might speak out my thoughts to you? I did whisper to him, "To you, revered Master, we are indebted for this magnificent laboratory. Your spirit, mysteriously conveyed to your successors in order, caused science—particularly chemical science—to so permeate the curriculum of Old Yale that the subterranean laboratory has been brought to the surface, enlarged, developed, and endowed, that its rays may illuminate the world—far and wide."

We chemists here assembled say to Yale that we are not envious—no, we are happy, felicitating you with all our hearts and with you thanking God that Silliman, the elder, was born.

To President Angell,

> As one arranges in a simple vase
> A little store of unpretending flowers,
> So gathered I these records of past hours,
> And trust them, kind Sir, to thy grace.

The Master of Physics Discusses Chemistry

[Resumé of Address by Sir J. J. Thomson]

Introduced to the audience of chemists assembled in Yale's large lecture hall as the most eminent of living physicists, Sir Joseph John Thomson, master of Trinity College, Cambridge, England, and discoverer of the electron, characteristically commenced his address with a laudation of J. Willard Gibbs, Yale's great pioneer in chemistry.

If we are to believe the newspapers, and even the statements of many scientists, epochs occur every few minutes, but, said Professor Thomson, with the most rigorous definition of epoch-making, Willard Gibbs's paper on "Equilibrium of Heterogeneous Substances" was the beginning of an epoch. Before the time of Gibbs, books on chemistry had only a few simple reaction formulas, but now chemical books bristle with differential equations which would be the despair of the older chemists. The subject of solution is completely covered by the additions that Gibbs made to the second law of thermodynamics.

Who is to say in this realm of physical chemistry what is physics and what is chemistry, Professor Thomson asked in stating that no wall of ignorance now separates physics and chemistry.

Physical chemistry is, however, dominated by thermodynamic considerations which are independent of the processes that go on. P varies with T, but that fact does not tell why T varies, and it is independent of the mechanism. Nor is physical chemistry by any means the whole of chemistry, Professor Thomson stated, pointing out that thermodynamical considerations play a minor part in organic chemistry.

The growth of chemistry up to the present point has been inductive, with little aid from theory. It is an excellent example of the progress made by able men without basic theory. To illustrate that theory is not all-important. No one who ever made a violin, a practically perfect musical instrument, had a theory of how it acted. We might even now know as much as we do about the motions of the moon and planets if the law of gravitation had not been discovered. Astronomers, by making long and patient observations in a manner similar to chemists, could have worked out the motions without the gravitation theory.

Chemistry has arrived at its present state without the material aid of the physicists. The chemist has wanted to know what an atom is but now the physicist is ready to tell him.

Professor Thomson told of the evolution of knowledge of the composition of matter which began with his discovery in 1897 that cathode rays are electrons. He graphically explained how electrons, equal in number to the atomic number, make up the negative part of each atom, and how there must be a central part of positive sign to counterbalance the electron.

When the physicist had finished determining the properties of his atom it strongly resembled the chemist's atom, and so far as it can be tested it is identical with that of the chemist. Just as during war time the laboratory process was subjected to service conditions before it was pronounced successful, so the physicist's atom has now reached the stage of practical testing by chemists. Professor Thomson believes that it will survive the strain of the chemist's practical test. That this adoption of the physicist's atom into the chemical family will benefit chemistry, he does not doubt.

We gasp at the diabolical syntheses of chemists expressed in milligrams. It is not underrating the sensitiveness of chemical tests to say that a millionth of a milligram of hydrogen can be detected; yet, if the chemist's test for a penny were no more delicate than his test for a molecule, the man possessing a million million dollars converted into pennies could not be distinguished by the chemist from a pauper.

Yet in physics it is easy to detect a single atom. By electrifying atoms they are placed under control because they can be given as much energy as desired, and energy counts in detection.

Professor Thomson urged the chemists to introduce physical apparatus into their chemical laboratories, stating that in no place would such an introduction be more appropriate than in the new Sterling Chemistry Laboratory at Yale.

Watson Davis

Science Service
Washington, D. C.

MATERIALS OF CHEMICAL-EQUIPMENT CONSTRUCTION SYMPOSIUM*

Papers presented before the Division of Industrial and Engineering Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923

Lead as a Material for Chemical Equipment

By George O. Hiers

National Lead Co., Brooklyn, N. Y.

LEAD, principally in the forms of pipe and sheet, is used very extensively in the chemical industries in the United States, chiefly in the manufacture of sulfuric acid and in the diverse industries using sulfuric acid.

Varieties of Lead

The lead used in chemical equipment in this country is almost entirely of a brand called "chemical" lead.

According to the tentative specifications for pig lead issued by the American Society for Testing Materials in 1922, commercial lead is classed in three groups—No. 1, corroding lead; No. 2, chemical lead; and No. 3, common lead. The following is quoted from these specifications:

> Chemical lead is a designation that has been used for many years in the trade to describe the undesilverized lead produced from southeastern Missouri ores. This lead contains from 0.04 to 0.08 per cent of copper, from 0.005 to 0.015 per cent (1.5 to 4.5 oz. per ton) of silver and carries less than 0.005 per cent bismuth.

These varieties of lead are often spoken of as "soft" lead in contradistinction to "hard" lead containing up to about 15 of antimony or lead hardened with other elements.

Properties of Lead

Lead is one of the metals which apparently has been serviceable to man from the earliest days. It is mentioned in the Bible and in other ancient writings. Although a common metal, lead has certain characteristics which make it very valuable in the chemical industries.

Softness—It is a soft, dense metal. Owing to its softness and lack of brittleness, in the forms of pipe and sheet it can readily be formed by bending or coiling without cracking. Sheets and pipes can be placed end to end or edge to edge, and welded or burned together forming a durable tight seam. The parts to be joined are scraped clean, and when placed together a bar of the same kind of lead is melted with an oxy-gas or an oxyhydrogen flame so that the three parts melt together. No flux is used. The ability to readily "burn" pieces of lead together is due to the fusibility of the metal. Lead melts at 327° C. (621° F.). Eight per cent antimonial lead, which is commonly used, starts to melt at 245° C. (473° F.) and becomes liquid at 296° C. (565° F.). Occasionally a lead-burner will make a futile attempt to join together two pieces of hard lead with a piece of soft lead. This is impractical or impossible; therefore, it is always recommended that on account of the same fusibility soft-lead bars be burned on soft lead, and hard-lead bars on hard lead. No advantage would be derived from burning soft lead to hard lead.

Malleability and Compressibility—The properties of malleability and compressibility account for the use of lead as valve packings and as gaskets or washers.

Sheet lead is made by rolling. A large ingot is cast, carefully skimmed, and cooled. The ingot is placed upon a roller table and fed back and forth between two large rollers, one or both of which may be power-driven. After many passes the relatively thick ingot is reduced to sheet of the desired thinness. Sheet lead is marketed according to its weight in pounds per square foot. The thickness in sixty-fourths of an inch corresponds closely to the weight in pounds per square foot. Eight-pound sheet lead is about $^{8}/_{64}$ or $^{1}/_{8}$ in. thick.

The pipe is made by a process called "extrusion." A cast ingot of lead in an iron cylinder containing a rod through the center, equal in diameter to the inside of the pipe desired, is forced by hydraulic pressure against a piston snugly fitting the cylinder. This piston is hollow and is rigidly fastened in the machine. At the end of the piston is a steel die with a circular hole equal in diameter to the outside of the pipe. The die is concentric with the core. From 10,000 to 60,000 lbs. per sq. in. pressure, varying with the cross-sectional area of the metal extruded, is applied to the lead.

Strength and Elasticity—Lead, as compared with other common metals, such as iron, steel, and copper, lacks strength. While no exact data are at hand, save the hardness tests cited below, it is known that the strength of lead decreases with a rise in temperature. It is often said that chemical lead will stretch when heated but will not contract again when cooled. This statement is true only in the event of the metal being stressed beyond its elastic limit at some time in the interval. With repeated alternate heating and cooling under too great a stress, the metal elongates. This elongation is loosely described as creeping or flowing of the metal. It should be borne in mind that any metal when stressed beyond its elastic limit at any temperature elongates permanently. A piece of soft lead of any uniform cross section and a length of 355 ft. could not be supported freely in a vertical position from the top only. It would elongate and break near the top under its own weight. This figure is derived by calculation using an ultimate tensile-strength value of 1740 lbs. per sq. in. Using a safety factor of five, as is found good practice in calculating the bursting strength of lead pipe, the safe limit of length of lead of uniform cross section supported freely in a vertical position from the top would appear to be 71 ft. at the ordinary temperature (25° C.). Since the metal is less strong at elevated temperatures, such as are commonly encountered in tall chambers, towers, or in deep tanks, the vertical sheets used therein should be given attention so as to prevent the metal from breaking under its own weight. There are two precautions that may be taken—the use of tapered sheet thickest at the top, or the use of straps on the outer sides to distribute the load.

Very little is found in the literature concerning the elastic limit of lead. Wertheim,[1] testing wires of small diameter in tension and taking as the elastic limit that force which

* Other papers forming a part of this symposium will appear in a subsequent issue.

[1] Burr, "The Elasticity and Resistance of the Materials of Engineering," John Wiley & Sons, Inc., 1905, p. 351.

will permanently elongate the metal 0.00005 of its original length, determined the elastic limit of lead as being from 284 to 355 lbs. per sq. in. for the annealed and drawn metal, respectively. Testing cast bars of metal 1 sq. in. cross section and 8 in. test length, the following results were obtained in an Olsen machine pulling the bars at the rate of 0.06 in. per min. The initial yield point was arbitrarily taken as 0.1 per cent elongation.

	Initial Yield Point Lbs./Sq. In.	Ultimate Tensile Strength	Total Elongation Per cent
Soft lead (S. E. Mo. desilverized)	328	1400	55
Hard lead (8 per cent Sb)	2664	7650	5

In testing 2-lb. sheet lead these results were found:

	Ultimate Tensile Strength Lbs./Sq. In.	Total Elongation Per cent
Chemical lead	2800	37
Hard lead (8 per cent Sb)	5500	15

Some $1^1/_4$-in. diameter extruded bars were tested with the following results:

	Ultimate Tensile Strength Lbs./Sq. In.	Total Elongation Per cent
Soft lead (S. E. Mo. desilverized)	1740	130
Hard lead (8 per cent Sb)	3340	75
Chemical lead	2300	50

Brinell hardness tests of different leads were made with these results for cast metal:

	25° C.	100° C.	125° C.	150° C.
Chemical lead	5.3	3.6	3.2	2.6
2 per cent antimonial lead	7.0	5.4	4.8	4.5
S. E. Mo. desilverized lead	4.2	...	...	...
8 per cent antimonial lead	13.0	...	...	...

STRUCTURE—Lead in the cast condition has a coarse, crystalline structure as compared with iron or brass. By rolling and extrusion the coarse-grain structure is broken up and a finer recrystallization takes place. Growth of the small grains in the worked metal occurs with annealing. In the course of a year, at ordinary temperatures, there is a slight grain growth in worked lead. Along or across the direction of rolling the grains due to recrystallization are apparently identical.

USE IN SULFURIC ACID INDUSTRY

Large quantities of chemical lead are used in the sulfuric acid industry. As is well known, sheet-lead walls are used in the chambers in the chamber process. In both the chamber and contact processes miles of pipe are used for conveying the acid about the plant and much sheet lead is used for making pans and tanks. Details of construction and use are described in some books on sulfuric acid manufacture.[2,3] Much valuable information is given in recent articles by French[4] and Jones.[5]

Sulfuric acid ranging in strength up to 60° Bé. (77.67 per cent H_2SO_4) has but slight action upon lead, even when heated to near the boiling point. When more concentrated (up to 96 per cent), the action is still only slight in the cold, but increases with rising temperatures.[2]

Hard lead will not resist the solvent action of hot concentrated sulfuric acid so well as chemical lead does, and is not recommended in contact with sulfuric at temperatures above 200° C. In lead chambers used in the manufacture of sulfuric acid the sheet ceilings and walls are carefully suspended. In many plants the wall sheets are fastened to the steel or wooden exterior structure or framework, with lead straps burned to the outside of the sheet. These prevent buckling and at times are used to support and distribute some of the load due to the weight of the sheet. The latter plan is highly commendable.

TANK LININGS

Large quantities of chemical and hard sheet lead are used to line the inside of tanks. The tanks outside are mostly of wood, but may be of concrete, brick, or structural steel. The use of lead-lined wooden containers was discussed by Dorr at the convention of the American Institute of Chemical Engineers, in his paper concerning the use of wood in the chemical industry.[6,7] Recently, cast hard-lead tanks about 2 ft. square by 4 ft. long have been produced and used. The sheet linings for tanks, vats, or other containers are made up of sheets seamed together by burning. This process was previously described, but is again mentioned because of its exceeding importance on account of its simplicity, and on account of making the metal especially usable. The linings overlap the top edge of the tanks, and may or may not be fastened, according to the necessity. Where solutions in lead tanks are heated by the injection of live steam, it should be directed away from the lead. To make lead last the longest in contact with hot corrosive liquids or gases there should be no hot spots in the metal—i. e., the metal should be at a uniform temperature. Occasionally, insects from a wooden tank bore through a lead lining. In such cases the insect or its eggs were present in the wood when installed. To prevent such trouble the wood may be treated with creosote. Before lining a brick or concrete tank with lead it is often recommended to put in a tar-paper lining.

OTHER LEAD EQUIPMENT

Stills are made from sheet-lead parts burned together. Some in use are 0.5 to 1 in. thick, and hold 50 gal. of liquid. In such cases no outside or inside reinforcement is used. Jugs, carboys, pails, and similar containers are constructed in the same way. Steam-heating coils of lead pipe are widely used, in heating corrosive liquids by immersion, in lead-lined or wooden tanks. Lead-pipe coils are used for cooling and condensing purposes. Special filter presses are made with lead. Lead pipe is extensively used for conveying corrosive liquids about a chemical plant.

On account of superior strength hard lead is employed in cases where it is sufficiently resistant to corrosion. "Crawl-proof" lead sheet is chemical lead reinforced with hard lead. Lead-covered and lined steel and iron articles are valuable as chemical equipment or in the construction thereof. Such products are on the market and have been found serviceable in the forms of pipes, fittings with or without flanges, valves, stirrers, agitators, tanks, coils, kettles, stills, pumps, evaporators, drying pans, drums, etc. The linings or coverings are of substantial thickness, and are preferably bonded or united to the iron or steel. Coatings of lead on steel and iron made by hot dipping, the Schoop or spraying process, and electroplating are somewhat thin. Terne plate or lead-tin alloy coating on iron is well known. During the recent war steel gas bombs were satisfactorily coated on the inside by electrodeposition. Lead, acting as insoluble anodes, is being used in the recovery of copper by electrodeposition from solutions.

The durability and cheapness of lead account for its wide usage in the chemical industries. In contact with many corrosive liquids or gases mentioned elsewhere, it has a long life. Many pieces of lead equipment in the chemical industry last for years. Corroding lead or common lead

[2] Wells and Fogg, *Bur. Mines, Bull.* **184** (1920).

[3] DeWolf and Larison, "American Sulphuric Acid Practice," McGraw-Hill Co., **1921**.

[4] *Chem. Met. Eng.*, **27** (1922), 219.

[5] *J. Soc. Chem. Ind.*, **39** (1920), 221T.

[6] THIS JOURNAL, **15** (1922), 94.

[7] *Chem. Met. Eng.*, **27** (1922), 1207.

containing several hundredths per cent bismuth is not recommended for chemical equipment. Some sulfuric acid solutions form an adherent protective coating of insoluble lead sulfate on the surface of the lead. Without erosive forces or abrasive action of precipitates in such a case, the lead lasts indefinitely. In the manufacture of sulfuric acid temperatures are sometimes high enough to melt the lead used. A manufacturer of dyestuffs used a cold solution of so-called sulfuric acid in a lead tank, which was quickly eaten away. It was later discovered that the solution contained considerable nitric acid. Such instances as these illustrate the difficulties encountered in attempting to predict how long a lead tank or other lead equipment will last. There is no doubt but that lead in chemical equipment is an economical material to use. It is used mainly in contact with sulfuric acid and solutions thereof. Various chemical industries having lead installations are: phosphoric acid manufacturers, color works, dye works, aniline works, perfume manufacturers, oil refiners, silk manufacturers, coke industry, glue, paste and adhesive manufacturers, manufacturers of hydrofluoric acid, hydrocyanic acid gas, boric acid, ether, soap, gunpowder, inks, phonograph records, graphite for pencils, straw bleachers. Some other uses are—in contact with alum solutions, photographic solutions, brine, pickling solutions, and electrolytes.

Effect of Impurities

In the last fifty years there have been numerous articles concerning the influence of impurities in lead. Such investigations have greatly advanced the art of using lead. Since lead is difficult to analyze and many of the investigators based their conclusions upon unreliable analyses, much of their work is of questionable value. In contending with this situation the American Society for Testing Materials[8] has published methods of analysis of pig lead, representing the best practice to date in this country. A table of analyses of varieties of pig lead follows:

Analyses of Pig Lead

(a) Southeast Missouri undesilverized
(b) Southeast Missouri desilverized
(c) Southwest Missouri undesilverized
(d) Ordinary common
(e) Ordinary corroding, or refined

	(a) Per cent	(b) Per cent	(c) Per cent	(d) Per cent	(e) Per cent
Silver	0.0070	0.0004	0.0005	0.0005	0.0005
Arsenic	Trace	Trace	Trace	Trace	Trace
Antimony	0.0030	0.0030	0.0020	0.0100	0.0050
Tin	None	None	None	None	None
Bismuth	0.0030	0.0030	0.0030	0.0800	0.0500
Copper	0.0600	0.0003	0.0190	0.0006	0.0006
Cadmium	None	None	None	None	None
Iron	0.0015	0.0015	0.0015	0.0015	0.0015
Zinc	Trace	Trace	Trace	Trace	Trace
Cobalt and nickel	0.0080	None	0.0018	None	None
Manganese	None	None	None	None	None
Total impurities	0.0825	0.0082	0.0278	0.0926	0.0576
Lead	99.9175	99.9918	99.9722	99.9074	99.9424
	100.0000	100.0000	100.0000	100.0000	100.0000

The (a) lead is chemical lead. It is produced from the sulfide ore, galena, in a blast furnace after roasting or in a Scotch hearth furnace, and refined without desilverization. The composition of this lead produced year after year is remarkably constant. The presence of copper is considered advantageous, whereas the other impurities are present in practically negligible amounts. With the modern intensive studies of corrosion and its nature, even greater usefulness of lead in chemical equipment may be predicted.

Acknowledgment

Acknowledgment is gratefully made to W. A. Cowan for his kind assistance in the preparation of this paper.

[8] Book of Standards for 1921.

Enameled Apparatus from a Chemical Engineering Standpoint

By Emerson P. Poste and Max Donauer

Elyria Enameled Products Co., Elyria, Ohio

ENAMELED metal for commercial operations is a rather recent addition to the list of equipment-construction materials, when considered along with such products as iron, copper, lead, or earthenware. The information regarding the properties of enameled ware and the possibility of coating with enamel the various shapes and sizes of industrial engineering pieces are consequently not as generally known or as fully understood as with older engineering materials. It should therefore be of interest to consider enameled ware from the standpoint of its resistance to the chemical action of industrial products and the controlling elements which determine the shapes and sizes possible.

Nature of an Enamel

The general conception of the inherent properties of enamel will be made more definite if we consider for a moment what constitutes an enamel. Perhaps the best definition for the equipment engineer is the one given by Popelin. It reads:

> Enamel is a glass fusible at a low temperature, and usually compounded of a mixture of borates and silicates. This mixture, originally colorless, combines with greatest ease with all, or almost all, metallic oxides under the influences of a pyrotechnic operation, thereby acquiring various bright or sober colors, according to the nature of the oxide, which the enameler can vary at will.

Varieties

This is a broad definition, but such a wide scope is necessary in order to cover the field of modern enamels. Many different kinds of oxides and different proportions of flux materials are used in making enamels. The manufacturer of enameled signs uses cobalt oxides for blue colors, chromium or copper compounds for green colors, and lead or antimony oxides for whites. A low-fusing, glossy enamel with brilliant colors is all that is required. Lead oxide is used in enamels for bathtubs and sanitary ware. When fused it presents a smooth surface with a wonderful luster. Such enamel has a very low acid resistance, being etched readily by the juice of a lemon. Smoothness to permit easy cleaning and resistance to water are its main requirements. The opacity in cooking ware is frequently obtained by using tin oxide or cryolite. Cooking utensils are subjected to the action of organic acids present in fruits and vegetables. The enamel must have greater acid resistance than bathtub ware. The oxides used may help to give greater acid resistance but they are chosen mainly because they are not poisonous. The proportions of borax, soda, and silica can also be varied so as to improve the acid resistance.

It is quite evident from these few familiar examples that the enameler can and has varied the nature of the oxides in enamel almost without limit, in order to obtain the results he desired. And the properties of the enamels have varied just as widely. These possibilities of variation present several points of interest to the equipment engineer who plans to use enameled ware in his processes. One cannot judge the serviceability of enamel for certain chemical conditions from the success or failure of another enamel under those conditions. This is especially the case when comparing a given enameled piece with another made primarily for an entirely different purpose. More important than this is the fact that enamels are varied or developed to meet certain conditions, and if the require-

ments are known it is quite probable that an enamel can be or has been developed for such conditions.

Enamels for industrial and chemical-engineering operations have been developed in this way. The demands of industry have dictated the general requirements. The enameler has varied the constituents of his formulas to meet these demands. The next step has been the preparation of the least number of different enamels whose chemical and physical properties overlap so as to cover the more important range of requirements. Thus, for fine pharmaceutical work and food work an enamel without heavy metals is required, and heavy metal oxides have been eliminated by most manufacturers of industrial enameled ware. There are many problems where a nonpoisonous enamel coating is desired to keep the product away from metal, and such enamels are available. If the product is a perishable food such as milk, it is, in addition, advantageous to have a smooth, glossy surface which can be easily cleaned and made sterile, and the glass-like surface of these enamels has been developed to a high degree. If the materials to be processed contain organic acids which gradually corrode metal, an enamel lining of a somewhat different character is needed. The enamel itself must have sufficient acid resistance so as not to be etched. It must cover the surface completely so that it does not expose the iron, even in an area as large as a pinhole, as that may be a starting point for action which will gradually increase the exposed area. There is a gradation of such acid materials starting with weak acids and continuing through to the most severe organic acids and to the inorganic acids, the latter being a great deal more corrosive. The stronger the acid conditions the more acid resistant must be the enamel. It must cover the metal completely and must present no irregularities in the composition of the enamel itself. For the strongest inorganic-acid conditions it is found preferable to apply the enamel as a powdered glass which is fused on the ware, because this permits a more acid-resistant base material. It is homogeneous when applied, preventing irregularities in the enamel coat itself, and also permitting a more perfect coating. It must be remembered that throughout this entire range of conditions the enameler is limited to materials which will fuse below the softening point of iron, and which have the proper coefficient of expansion compared with iron so that the enamel will adhere properly. Such limitations make the problem of meeting the chemical requirements with a suitable enamel much more difficult than if these restrictions were not imposed.

Enameled equipment coated with a lining which has been developed primarily to avoid contact with metal is used for industrial work of the following nature: In food work, for example, milk and ice-cream products are mixed, pasteurized, and stored in such vessels. Sugar sirups and beverages are mixed and stored therein. Along chemical lines, vegetable oils are refined, deodorized, and stored in appropriately designed enameled units. Ammonium nitrate is crystallized in enameled crystallizing pans. Phenol is stored in tanks with such an enamel coating. These are but a few typical examples for which it is perfectly obvious that protection from metallic contact is desired, but beyond that there is no great acid action.

As typical of materials requiring more acid resistance than those above, fruit juices, such as grapefruit juice, are stored in enameled vessels having good resistance to organic acids. Citric acid-beverage sirups and especially beverage-flavoring concentrates containing large amounts of citric acid are mixed and stored in such tanks. Tincture of iodine, chlorinated water, and other chlorinated products are made in such equipment. Aspirin is made in enameled units of this class. Various photographic developing chemicals are made and crystallized in similar equipment. This enamel can also be used for storing tin chloride or zinc chloride containing a slight excess of inorganic acid.

Inorganic acids have a much more severe corrosive action on enamel itself than the materials so far listed. Also, even the slightest imperfection makes the equipment unfit for use. Such conditions have been satisfactorily met by enamels of the highest acid resistance. As we have previously mentioned, the enamel is usually applied by dusting onto the hot metal piece, or occasionally the moist sprayed piece is dusted over with powdered enamel. Typical problems for such enamel are the evaporation of aluminium chloride, copper chloride, or silver nitrate containing excess acids, the refluxing of organic compounds with nitric or hydrochloric acids, or the dissolving of platinum in aqua regia.

Behavior under Varying Conditions

It is quite evident that enamels may vary greatly in their ability to resist corrosive conditions. In the same way a given enamel may resist acid action quite differently under varying conditions. It has been found possible to get some idea of the resistance of enamels under changing conditions by subjecting a weighed amount of powdered enamel frit to the action of the corrosive solution and then filtering off and weighing the residue. An enamel which is somewhat susceptible to the action of the material must be taken if the effect of various strengths of the same solution is to be noted, as otherwise the figures will all be uniform. Also, the results do not represent the resistance of the enamel on the ware as the powdered frit is in a different condition from the fused enamel on the finished piece. The accompanying graphs are results obtained from such a study. Fig. 1 shows the relative corrosive action of acetic, hydrochloric, sulfuric, and nitric acids of various strengths on the same enamel frit. It will be noted that the action is much more severe where the ion concentration is greatest. Moreover, an organic acid such as acetic acid is much less corrosive than inorganic acids.

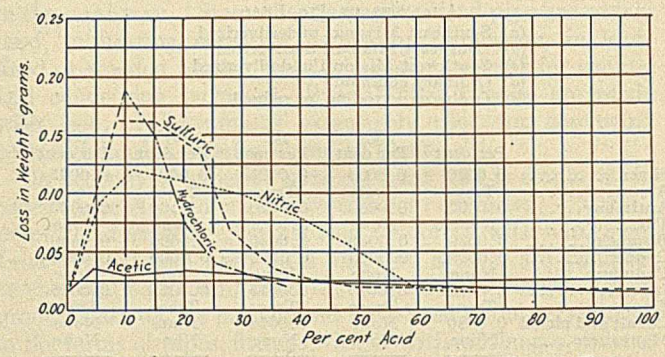

Fig. 1—Action of Different Acids on the Same Enamel Frit

In Fig. 2 three different enamel frits were subjected to the action of sulfuric acids of various strengths. The three frits represent more or less the three different classes of industrial enamels heretofore discussed. According to the curves an enamel represented by Curve II would be satisfactory for cold sulfuric acid at 50 per cent strength, but entirely impossible for 15 per cent acid. The enamel represented by Curve III would be entirely satisfactory for either case. Under the conditions of the test, the Frits I and II were entirely out of range near the point of maximum activity, as all the acid-soluble material had been removed. The dotted lines show the probable nature of the curve which would result if this had not been the case. The tests were carried out at room temperature. If higher temperatures were used the general nature of the curves would be the same, but the degree of action would be greater. This change would be

more pronounced with Frits I and II than with the more acid-resistant Frit III.

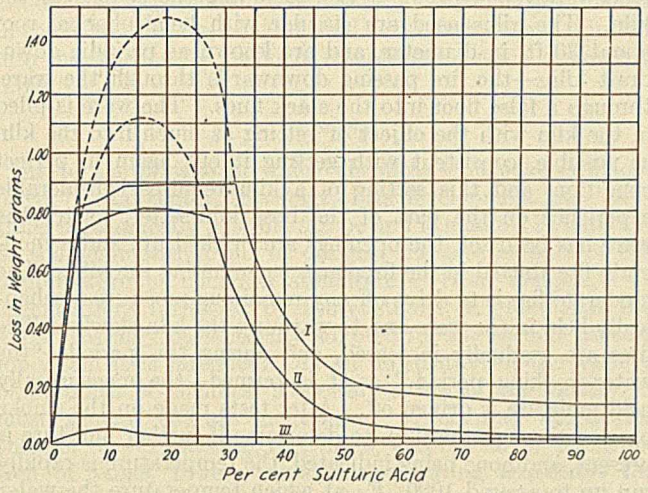

Fig. 2—Action of Varying Strengths of Sulfuric Acid on Enamel Frits of Different Acid Resistance

As we have said before, such curves do not represent the resistance of an enamel to acid corrosion, because for the enamel which is to meet the entire range of conditions the graph would be practically a straight line. On the other hand, from such curves it is possible to judge which conditions are most corrosive toward enamels, and one can be guided in the selection of a proper enamel.

Alkali Resistance

Perhaps a statement should be made regarding the alkali resistance of enamels. In general, enamels are acid materials with silica as the main acid. Their acid resistance varies according to the ion concentration of the acid solutions involved. Enamels which have been developed to meet certain conditions may or may not resist other conditions, and the chemical nature of the solutions involved must be considered. When we come to alkali resistance of enamels we must look at them from the same point of view. Most industrial enamels will resist ammonia or alkali carbonate solutions as they have no strongly basic reaction. Free caustic soda in solution, especially if hot, will etch or decompose enamels. Some salts, such as sodium sulfide or potassium cyanide, which have a strong alkaline action in solution will also etch enamels. Contrary to the usual opinion, the enamels higher in silica which are most acid-resistant also have the greater resistance to alkali.

Problems in Applying Enamel

The fact that an acid-resistant enamel is more resistant to most other conditions often prompts the question—why not use this enamel on all equipment and have it one standard grade? This brings us to the problem of considering the nature of the limitations of applying enamel to industrial equipment of various shapes and sizes. The enamel is usually applied in one or two different ways. It may be ground up with water and a small amount of colloidal clay, the latter keeping it in suspension. The enamel in this form is sprayed over the surface to be enameled. It is dried. The tank is then put into a heated furnace and brought to a red heat to fuse the enamel. Several coats are required to build up a uniform surface. This system is much the same as that used for cooking ware, except that the small steel shape can be dipped, then drained, dried, and burned. The other system of applying enamel is to cover the iron with a wet, ground-coat enamel as above, to protect it from oxidation The piece is put into the furnace and when red hot is taken out and powdered enamel dusted uniformly over the piece by means of a mechanically agitated sieve. The piece is then returned to the furnace while still hot, and is heated until the enamel has fused down uniformly. The enameling of bathtubs is done in very much the same way, but the enamel used is much softer and fuses at lower temperatures than enamel for chemical equipment.

The enamel itself is a thin layer of glass and must be considered as such. It cannot be applied over sharp corners without having strains which will later cause the enamel to jump. A piece such as a plain pipe end cannot be enameled over the edge and be sure the enamel will cover it thoroughly and be acid-resistant. Surfaces to be enameled should be of simple, uniform contour. There should be no projecting ledges on the inside of a tank which is to be covered with enamel. The piece should have a fairly uniform thickness. Parts should not overlap one another so that one shades the other from the furnace heat, because the piece should heat up uniformly when the enamel is being fused. Shapes must be such that the enameler can spray or slush the moist enamel uniformly over the surface to be covered. Where the dusting process is used the unit to be enameled must have a plain, open shape so that the powdered enamel can be quickly and uniformly applied.

A softer enamel of the less acid-resisting type can be applied to more varied shapes than the harder varieties. It has a more uniform covering power and produces a finished job with less effort. It may fuse down more uniformly. It has greater elasticity and may resist heat shocks more easily. Where it is a matter of merely covering the surfaces to prevent metallic contact, it is preferable to use an enamel of that type.

In enameling a vessel for organic acids other problems present themselves. The enamel itself must be more acid-resistant. The unit must be designed so as to permit perfect enameling of the entire inside surface. The determination of such limitations is dependent on various conditions learned only by experience. In general, the simpler the design of such a piece, the more easy it becomes to get a perfect coat. The sizes are usually limited from 500 to 1000 gal., depending on conditions, as it has been found that beyond those sizes the difficulties of manufacture become increasingly greater.

Enamels that are dusted on the hot piece can be applied only to simple, open shapes. The process of applying the enamel is essentially a hand operation and this limits the size of piece which can be properly handled. The limiting figures vary, some manufacturers stopping at 300 gal., while others produce pieces of 500-gal. capacity.

Conclusion

It has been our aim, in the foregoing paragraphs, to give the manufacturer who uses equipment an idea of the differences between various classes of commercial enamels and how they have been developed to meet different requirements. It is impossible to study the acid resistance of enamels as a class, because enamels have been developed to meet the chemical requirements given and the range includes enamels which are resistant to most acid conditions encountered. As the severity of the acid corrosion becomes greater it is necessary to limit the size and shape to a greater extent to insure a unit with a perfect enamel coating which will give good service for the operation in which it is to be used. The enameler is developing his ware more and more to meet the requirements of industry and the limitations are growing less in proportion. Industrial enameled equipment is consequently finding an increasing field of service in chemical and industrial engineering work.

Acid- and Chemical-Proof Stoneware

By M. A. Knight

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CHEMICAL stoneware is a ceramic material made from specially selected clays and fired to the vitrification point. Properly manufactured chemical stoneware does not rely on a glaze, enamel, or veneer for its resistance to corrosive acids and chemicals, but the entire body throughout should be resistant. On such ware a plain salt glaze is put on for appearance but plays no part in the wearing qualities. The salt glaze is applied by throwing salt on the kiln fires at their highest heat, which breaks up the salt, and the sodium combines with the clay on the surface of the ware to form sodium aluminium silicate, giving a smooth appearance and a neat look to the ware.

The clays as used for chemical stoneware (more than one clay is used and the clays are blended before using) are nearly pure aluminium silicate with but small traces of lime, magnesia, or iron. They should, for most of the product, be also of the plastic type so they can be readily molded. For the various types of bodies produced to meet the various demands in the chemical industry, various types of clays from different parts of the United States and foreign countries are used, and blended as required.

Manufacture of Chemical Stoneware

The clays as received in the raw state are ground, washed, sieved, filter-pressed, and then blended and mixed and ground in a special machine for that purpose. The blends are then put into aging pits of concrete where they age for various periods. After aging the clays are ready for the workmen.

Chemical-stoneware manufacture differs from ordinary stoneware, porcelain, or sewer-pipe manufacture in that in chemical stoneware but very little machinery is used. The principal use for machinery in chemical stoneware is in preparing the clays, after which the work is almost entirely hand work by skilled men who must know how to read and interpret a blueprint. In the other ceramic industries as much of the manufacturing is done by machinery as possible; hence, they are "quantity" producers, whereas chemical stoneware is "quality" production. Machines for making chemical stoneware have been tried but so far have not been found as satisfactory as hand production.

Orders for chemical stoneware are often accompanied by blueprints or special specifications, which are turned over to the proper department in the plant devoted to the group in which the design belongs. The job is then assigned to a specific workman, who proceeds, from the clay already prepared and of the proper body, to mold the piece of ware in accordance with the blueprint or specifications. The time required for molding may be hours, days, or weeks, depending on the size and the design. When the piece has been molded in accordance with the specified design, it is ready for the drying.

Drying is accomplished in three ways—by natural air drying, in heated large rooms, and in automatic tunnel driers. Each has its specific use in accordance with the design, size, and thickness of the piece. Drying is one of the critical periods in the passage of the piece through the plant. The ware must be dried from the inside out, not from the outside in, or stresses will be set up in the structure which will later develop trouble in the firing. Also, the drying must not be too fast, for the same reasons. The clay shrinks about 5 per cent in volume during drying so this shrinkage has to be taken into account when molding the piece.

When the piece has been thoroughly dried both inside and out, it is ready for the kilns or firing. Firing in chemical stoneware requires two weeks, including the cooling of the kiln. The kilns used are circular with hemispherical roof about 30 ft. in diameter, and are known as periodic downdraft kilns—the fire passing downwards through the ware, through a false floor into the stack flues. The ware is piled in the kiln with the object of getting as much into the kiln as possible, consistent with getting it out again in perfect condition, and this setting of a kiln requires considerable experience on the part of the boss kiln-setter. After the ware has been set, the openings are bricked up, and a moderate fire started in the fireplaces surrounding the kiln. The moderate fire is to drive off any remaining moisture mechanically held in the ware and to warm up the kiln slowly. The fires are gradually increased, and during this period—"the water-smoking period," as it is termed—the mechanically held moisture is driven off. After tests made on the smoke passing through the flues to determine if further moisture is present, and none being indicated, the temperature is rapidly run up to around 1000° F., at which temperature the water of crystallization of the clay is driven off, the temperature being held at this and a slightly higher point for a predetermined time. (The recording pyrometers used indicate the general time.) This converts the clay into stoneware, but as far as chemical stoneware is concerned the firing is but half completed. After the temperature for driving off the water of crystallization has been held for the proper period, as mentioned above, the fires are crowded to their limit and the temperature gradually pushed up until it reaches the neighborhood of 2500° F., when complete vitrification or fusion of the body of the ware takes place. After this point is reached and held for a certain period, the fires are permitted to die down slowly, and when sufficiently low the fireplaces are bricked up and the entire kiln allowed to cool slowly by natural radiation. Thus, the ware is cooled slowly or, in other words, annealed, producing tough, strong structures which will withstand considerable rough treatment.

When the kiln is cooled off, the ware is removed from the kiln, taken to the warehouse, inspected, tested, checked, and packed for shipment.

Advantages and Limitations

In all industries where corrosive chemicals are manufactured or used it is a necessity that the apparatus constituting the plant equipment be of materials that will withstand the action of the chemicals, for two reasons—first, on account of the excessive cost of constant replacement of apparatus, and second, on account of the contamination of the manufactured product due to the corrosion of the apparatus. On this account chemical stoneware was developed, as of all the materials offered for this kind of work it is probably the most versatile one in that it is practically immune from the attacks of most every chemical and acid except hydrofluoric acid, which acts on the silica in the clay. Of course, chemical stoneware also has its limitations and is not the Utopia in acid-resisting material, but for general all-round use there has still to be found a better material. The limitations of chemical stoneware are briefly—limits as to size in which it can be made, tensile strength as compared to the ordinary metals, and heating by direct flame cannot safely be done. To overcome the first limitation has been the aim of the manufacturers of chemical stoneware ever since they have been in business, with the result that every year larger and more complex pieces are produced, some reaching a capacity of 1000 gal. and over. To overcome the second, constant experiments are being conducted to improve the strength of the body, with the result that we

have to-day ware that will withstand in some cases more punishment from mechanical injury than some of the compounded ferrous alloys. For the last, heating is substituted in the form of water, oil, and sand baths, or by steam injected into the solution by means of chemical-stoneware perforated pipes.

Designs

As to the designs in which chemical stoneware is made, it can be said that at this stage of its development most anything mechanically possible can be and is made. In addition to the commoner forms or designs, the greater part of the manufacture of chemical stoneware is from blueprints or specifications furnished by the customer in order that the apparatus may be especially adapted for the specific process for which it is intended. As an illustration of the variety of products of chemical stoneware a few of the variety in most general use are mentioned: towers and accessories therefor; tower packing; tile, brick, and blocks for construction of tanks, towers, vats, etc.; elevating apparatus for acids and corrosive liquids; acid receivers and tourills in the manufacture of acids; kettles, with or without stirrers; gas generators; arsenic acid generators; jars; decanting jars; subliming pans; tanks; laboratory sinks; filters; coils; manifolds; pipe and fittings in many styles and bores, return bends; S-pipe, vapor pipe; sleeve pipe, troughs, pipe dampers; faucets, cocks and valves; carboy stoppers; pitchers, jugs and buckets; dipping baskets, funnels, burner guards; Mariotte jars, etc. In other words, the field of requirements of the chemical and allied industries is practically covered. Specific mention may be made that chemical stoneware is used in plants manufacturing acids, alkalies, explosives, dyestuffs, chemicals, pharmaceuticals, fertilizer, vinegar, foodstuffs, and mineral products, and for plating, lithographing, developing, and pickling processes.

Types of Bodies

It has been stated above that various types of bodies are produced to meet the needs of the different classes of equipment. It is not to be understood that there are an indefinite number of bodies in general use, but rather that a reasonable number are employed. To be specific, the bodies employed by one manufacturer may be referred to as Nos. 1, 2, 3, 4, 5, 6, and 7.

No. 1 is a porous, open body, through which liquors will readily run, but which will hold hot acid gases. Finished unglazed, it serves for such uses as carboy stoppers, filtering plates and cups, electrolytic diaphragms, or any pieces subject to high temperatures and sudden changes.

No. 2 is a semiporous, open, rough body, through which liquors will seep, but which is excellent for hot gases and for sudden changes in temperature. It finds use in baffle plates, heavy tile, covers and blocks for furnaces, and large pipe for hot gases. It is finished either glazed or unglazed.

No. 3 is a fine, close-grain structure, through which liquors are apt to sweat, but which is good for hot liquors and gases and uneven heat action. It is used for standpipe or fittings next to furnaces, muriatic acid sleeve pipe, boiling kettles, hot towers, burner guards, ejectors, and steam jets, and is finished smooth, bright, and glazed.

No. 4 has a tough, rugged, vitrified structure, not as close and fine a body as No. 3 or No. 5, but more vitrified and denser than No. 2. It will hold acid without seepage, and is used for large pieces of 250-gal. capacity and over, for large tower pipe, kettles, and blow-cases, grillage tile, brick, heavy tanks. It is good for ordinary heat changes in temperature and is finished glazed and somewhat rough.

No. 5 has a close, dense, fine structure. This can be considered the general average body. It will withstand ordinary temperature changes but not sudden changes. It is finished smooth with a bright glaze and is used for receivers, tanks, jars, drainage pipe, tourills, evaporating pans, condensing pipe, sinks, and arsenic equipment.

No. 6 is very fine, close, vitrified structure—closer and denser than No. 5. It will not stand heat action as well as the bodies previously described. It is used for acid pitchers, monkey pumps, laboratory sinks, vacuum filters, funnels, flanged pipe, coils, tanks, jars, and other pieces where heat changes are small and slow. It is good for storage vessels, etching machines, chlorine pipe and fittings, etc. It is finished bright, clean, and smooth, with a heavy glaze.

No. 7 has a very fine, tight, close body, vitrified to almost a glass texture. It will not withstand changes in temperature or high temperature, but with this body there is no absorption whatever. It is used for valves, faucets, cocks, pebble-mill jars, distilled-water jars, small bore pipe and fittings, or any small pieces up to 50-gal. capacity where there is very little heat action. It is finished very bright, smooth, with a glazed surface, and made up into only thin, light-weight, or small pieces.

General Characteristics

A few words about the general characteristics of chemical stoneware are in order. At first it was deemed necessary to make walls of apparatus heavy and thick, for mechanical strength as well as for resistant purposes. The present tendency is to make the walls as thin as possible, and it is surprising to note how thin they are made and yet combine strength and immunity to corrosion. In addition to the fact that the thinner walls make the apparatus lighter, they carry also the property of being better able to withstand the action of heat and cold (expansion and contraction) and permit better radiation of heat in the case where heating is to be done or solutions are to be cooled off. It is the practice with chemical stoneware, where there is alternate heating and cooling, to avoid designs having sharp edges or corners, and to substitute rounded designs, since, inasmuch as chemical-stoneware bodies are of a crystalline nature and therefore require time for the molecules to adjust themselves to changes in temperature, the square design or sharp corners do not permit of even expansion or contraction and hence increase the liability to cracking. In this respect it should be mentioned that it is not the *degree* of heat or of cold to which the ware is subjected that has to be guarded against, but the *suddenness* with which the change from hot to cold or cold to hot is made, as well as the evenness with which heat or cold is applied.

Where chemical stoneware apparatus to an *exact* measurement is required, this is obtained by having the piece run slightly over in measurement and then grinding back to measurement. However, this is a long, tedious, and expensive operation, requiring the use of carborundum and machinery, and if exact measurements are not an absolute essential it is better to avoid this expense. Chemical-stoneware bodies are so hard and tough that nothing softer than carborundum will cut them with economy, and then only at a comparatively slow rate of speed.

Time Required for Manufacture

The time required to manufacture chemical-stoneware apparatus varies with the size, design, and thickness of the piece, and runs from four to ten weeks. The greater part of the time is consumed in the drying and the firing of the piece, and in those two stages the time cannot be shortened with safety, no matter how necessary it may be to get the piece out faster. Hurrying the manufacture during drying or firing usually means the entire loss of the piece, with the result that the work must be started all over again from the beginning with consequent still longer delay. It is therefore best to allow as much time as possible for manufacture when preparing plans for new installations or the repair or replacement of old.

Hard Rubber and Its Application in the Chemical Industries

By A. C. Buttfield

American Hard Rubber Co., Butler, N. J.

IN PRACTICALLY every chemical plant there is some process or reaction where a corrosive reagent of one kind or another is used or produced. The selection of a suitable material for the containing and conveying of such a reagent is one of the important problems confronting the chemical engineer, for upon the proper selection may depend the success or failure of the entire enterprise.

A great number of noncorrosive materials have, from time to time, been brought to the attention of the engineer, and as no single one of these will serve to solve every problem, it is necessary to carefully consider all before a final decision is reached. The material with which this paper is concerned and which, though used to some extent for many years, has recently aroused an increasing amount of interest, is hard rubber.

Nature of Hard Rubber

As the average person has but a rather imperfect conception of the nature and composition of hard rubber, a brief description will, perhaps, be not out of place. Essentially, hard rubber is rubber compounded with a relatively high percentage of sulfur and cured for a comparatively long time at a relatively high temperature. While the line of demarcation between hard and soft rubber is not sharply defined, it is approximately correct to say that the sulfur content of hard rubber ranges from 15 to 50 per cent of the combined weight of the rubber and sulfur, the average being in the neighborhood of 30 per cent. Upon this factor—the ratio of rubber to sulfur—depends, to a large extent, the hardness and other properties of the final product. Of course it is possible to vary the hardness by limiting the cure, but in general this has been found to be bad practice, for incompletely vulcanized rubber is less stable than the properly cured product.

Another means of changing the properties is by compounding the rubber with materials other than sulfur, and in this respect hard rubber resembles soft rubber; for just as pure rubber and sulfur, while excellent for such articles as elastic bands, would nevertheless be of but little value for automobile tires, so hard rubber containing nothing but rubber and sulfur, while excellent for making fountain pens, would be worthless for certain magneto parts. In this compounding experience and skill play an enormous part and upon the proper use of the right ingredients largely depends the value of the final product. Thus, it will be seen that the physical properties may be changed by varying the mixing and cure, and these changes, when properly controlled, make it possible to modify or increase the relative value of the resultant properties, so that the finished article may be most suited to the service intended.

With this explanation in mind, it will readily be understood that it is impossible to set down fixed physical properties for hard rubber. The following will, however, serve as a guide:

Tensile strength	1500 to 10,000 lbs. per sq. in.
Compressive strength	3000 to 20,000 lbs. per sq. in.
Elongation, from 2 per cent in the harder, to 75 per cent in the softer grades	
Specific gravity, 1.14 upwards. Average about 1.20	
Scleroscope hardness, 35 to 65	
Effect of heat—all but the specially hard grades soften noticeably at 160° F.	

For this reason hard-rubber chemical apparatus is not generally recommended for temperatures over 130° F.; not because its resistance to corrosion is reduced, but rather because deformation is liable to take place.

Hard rubber is nonporous, nonabsorbent, nonhygroscopic, and odorless. It may be machined, cut, threaded, sawed, ground; in fact, it resembles a metal in these respects. It is capable of taking a beautiful high polish; metal inserts may be molded in it and metal objects covered with it.

Hard rubber has some remarkable electrical properties. Its dielectric strength runs as high as 1000 volts per mil, and its insulation resistance (resistivity) ranges up to 12,000,000,000 megohms per centimeter. Tests made by the Bureau of Standards have shown a grade of hard rubber, prepared especially for radio work, to have a lower inductive capacity and phase angle at radio frequencies than eleven other well-known materials.

Hard rubber of suitable compound is chemically inert to a high degree and is successfully used in connection with a great many corrosive materials. Many laboratory tests have been made in which hard rubber has been immersed in various chemicals for long periods of time, and it would be possible to present many tables showing the effect of these chemicals in terms of loss or gain in weight per unit of surface. Such tables are often misleading, however, and it has been thought preferable to enumerate some typical materials in connection with which hard rubber has actually been commercially used for years. A few of these are: sulfuric acid of not over 1.50 specific gravity, nitric acid of not over 1.12 specific gravity, hydrochloric acid of any concentration; acetic, hydrofluoric, hydrofluosilicic, and phosphoric acids; sodium and potassium salts, such as hydroxides, chlorides, sulfates, etc.; zinc chloride, ferric chloride, stannic and stannous chlorides, calcium chloride, and many others, as well as corrosive gases, such as chlorine, hydrochloric acid gas, etc. Hard rubber is attacked by most rubber solvents, such as benzene, carbon disulfide, and chloroform, which tend to soften and swell it.

Equipment Obtainable

A very large variety of hard-rubber chemical equipment is obtainable. Pipe ranging in size from $^1/_8$ to 4 in. is regularly supplied, while larger sizes can be made. Fittings such as elbows, tees, unions, flanges, bibb cocks, valves, strainers, and ball floats are stocked, all with standard pipe threads, so that complete conveying lines can be readily assembled. Pumps, both reciprocating and centrifugal, in which all parts coming in contact with the solution to be circulated are either of solid hard rubber or metal entirely protected by seamless hard rubber, are made in sizes having capacities of from 6 to 122 gal. per min. A complete assortment of utensils, including buckets, measures, dippers, funnels, jars, baskets, scoops, etc., is available. Tanks of solid hard rubber as large as 15 ft. in length have been made, and such tanks can be supplied in almost any desired shape. Another adaptation of hard rubber is its use for lining or covering metal objects, such as iron tanks, centrifugal extractors, pipes, agitators, etc. By a recent discovery it has been found possible to improve upon the usual practice of placing the hard rubber in direct contact with the iron, by first applying a layer of special soft-rubber compound, and then covering this with a layer of hard-rubber compound, the whole being vulcanized together. The soft rubber not only adheres to the iron much more tenaciously than will hard rubber, making separation of the tank and lining almost impossible, but also acts as a shock absorber and compensates for differences in expansion due to temperature changes, thus protecting the hard rubber from possible fracture.

In addition to the articles mentioned, much hard rubber in the form of sheet, rods, and tubes is used in various chemical

industries, as well as molded articles of many special sizes and shapes.

Industries Using Hard-Rubber Equipment

A complete list of industries in which hard-rubber equipment is used would be too long to fall within the scope of this paper. A few installations will be briefly described which will serve as a general guide for those who may be interested.

Hard rubber is used perhaps most extensively for handling hydrochloric acid of various strengths. Installations of this kind include apparatus for conveying the acid from tank cars to storage tanks. This is done in three ways—first, by blowing with compressed air from the car through hard-rubber distributing lines; second, by pumping, using hard-rubber pumps and distributing through hard-rubber piping; third, by siphoning through hard-rubber pipes to hard-rubber air lifts, which raise the acid to tanks for distribution.

Hard-rubber pumps and piping are also used in connection with hydrochloric acid for the extraction of rare metals from their ores; in the manufacture of galvanized iron wire, and like products; by dye manufacturers, who find hard rubber excellent for conveying acid through various steps in the manufacture of dyes. Special parts, such as dipping baskets, air-agitator systems, solid hard rubber and hard-rubber-lined tanks, are used extensively by metal-etching concerns. This equipment is also suitable for dilute nitric acid, ferric chloride, and other solutions used for etching purposes.

Various manufacturers use thousands of feet of hard-rubber pipe for siphon systems on nitric acid absorption towers. These systems are used from the first tower in the series through to the point where the nitric acid concentration exceeds 16° Bé.

One of the largest single uses of hard-rubber equipment is in the silk-dyeing industry for handling stannic chloride solutions used in weighting silk. Typical installations include mixing tanks for building up the tin content of the spent tin solutions and soaking tanks where the silk is soaked in the solution until the required weight has been taken on. In the so-called "dynamiting" process, the tin solution in a continuous system is pumped by hard-rubber pumps into a constant level hard-rubber-lined tank, which in turn feeds hard-rubber-lined and covered centrifugal extractors which are filled with silk for weighting purposes. The solution passes through the silk fibers and is discharged into a hard-rubber-lined collecting tank, from which it is again pumped to the constant-level tank. The liquid is fed to the extractors for a definite period of time, this time being calculated to produce a certain amount of extra weight per pound of raw silk.

Hard rubber is used in large quantities in the manufacture of chlorine and hypochlorites by the electrolytic process, as piping for distribution of the chlorine gas from the cells and for collecting the hypochlorite liquor. Concerns engaged in the manufacture of chlorine often furnish hard-rubber distributing lines with their chlorine containers. These lines convey the gas direct to bleaching processes in various industries, many of which use agitating systems forcing the gas through hard-rubber pipes drilled with small holes and immersed in tanks containing the material to be bleached. Chlorine control apparatus for use with flour and cotton-bleaching processes is often of hard-rubber construction. Here hard-rubber towers, float balls, and various forms of special equipment are indispensable.

An interesting development in the use of hard rubber is shown in the handling of plating solutions, many of which have a tendency not only to corrode, but also to form deposits on the surfaces of metallic containers. Hard-rubber goosenecks, electrode separators, and tanks are used in general plating work, the tanks serving to reduce electrical leakage to a minimum, owing not only to the high insulating properties of hard rubber, but also because there are no pores in which the solution may crystallize as it does, for instance, in the cellular surfaces of wooden tanks.

Many installations of hard-rubber equipment have been made in plants devoted to the manufacture of food products, where its resistance to corrosion and its nonporous and nonabsorbent properties make it ideal for handling such material as cider, fruit juices, vinegar, etc. Cider and vinegar plants use hard rubber very extensively, not only as pumps, piping, and fittings, but also in the form of special filtering apparatus, tilting vessels, and special distributors or sparges which are used in every vinegar generator.

Condiment manufacturers use hard-rubber pipe, fittings, tanks, and special apparatus throughout their mixing and other processes, and even through to the point where the condiments are bottled.

Very interesting results have been obtained recently in connection with experiments in the transportation of hydrochloric acid by means of hard-rubber-lined iron tanks mounted on tank cars. These experiments, while not yet altogether successful, show promise; and it seems probable that they may be carried on to a successful conclusion.

Many other uses of hard-rubber equipment might be described, but those mentioned will serve to give a comprehensive idea of the wide range of usefulness of this unique material, and to show that it is worthy of consideration wherever the handling of corrosive substances prevents the use of the more common materials of chemical-equipment construction.

New Haven Registration

The registration, by states, of those present at the New Haven meeting was as follows:

Arkansas	2	Louisiana	4	Oklahoma	1
California	7	Maine	1	Omaha	2
Colorado	2	Maryland	18	Pennsylvania	72
Connecticut	145	Massachusetts	108	Rhode Island	13
Delaware	25	Michigan	14	Texas	5
District of Columbia	63	Minnesota	5	Vermont	7
Georgia	2	Missouri	7	Virginia	7
Illinois	38	Nebraska	1	Washington	1
Indiana	7	New Jersey	13	West Virginia	8
Iowa	1	New York	265	Wisconsin	8
Kansas	4	North Carolina	4	Foreign	16
Kentucky	1	Ohio	56		
		Guests	218		
		Total Registration	1151		

Committee on Standardization of Cuprammonium Method for Viscosity of Cellulose

The American Chemical Society, through its Cellulose Division, has appointed a committee to standardize the determination of the viscosity of cuprammonium cellulose solutions as a control method. This committee is desirous of obtaining the coöperation of all individuals or firms who are interested in the cuprammonium method for viscosity of cellulose. It is generally agreed that the method is of considerable importance in the cellulose industry, and no doubt there is considerable information available from widely scattered sources. The committee is anxious to obtain the assistance of anyone who is willing to coöperate on this matter. Descriptions of methods now in use, together with comments as to possible means of improvement, or general discussion of the method and the results obtainable by it, will be welcomed by any member of the committee.

The members of this committee are:

L. O. Littleton, Massasoit Mfg. Co., Fall River, Mass.
E. F. J. Puckhaber, Stamsocott Co., Hopewell, Va.
C. S. Venable, Viscose Co., Marcus Hook, Pa.
W. O. Mitscherling, 2018 Jefferson St., Wilmington, Del

MOTOR-FUEL SYMPOSIUM

Papers presented before a joint meeting of the Divisions of Petroleum Chemistry and Gas and Fuel Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923

Fuel Requirements of Internal-Combustion Engines[1]

By Stanwood W. Sparrow

Bureau of Standards, Washington, D. C.

OVER twelve million automobiles are in operation in this country. Evidently, the "fuel requirements of intercombustion engines" have been met whether they have been understood or not. It would be easy to state the characteristics of a satisfactory fuel. This discussion attempts something more difficult—namely, to suggest *how* various characteristics of a fuel affect its ability to fulfill the requirements of internal-combustion engines. In what follows fuel has been considered from the standpoint of (*a*) availability, (*b*) usability, and (*c*) power-producing ability.

Availability

To burn a gallon of alcohol one thing is essential—namely, a gallon of alcohol. No discussion is necessary as to this phase of availability, nor is there any doubt that availability means available on a commercial scale at a reasonable price. But availability means more. It means that fuel available in New Haven to-day should be available in New York to-morrow and in Detroit next week. Why? Consider alcohol. To use alcohol as a fuel carbureter jets must be larger than when gasoline is used. Making the carbureter right for alcohol makes it wrong for gasoline. It may be relatively easy to use either alcohol or gasoline as a fuel. It would be extremely difficult to use first one fuel and then the other. There is still another angle to this question of availability. In citing the advantages of fuels such as alcohol and benzene, stress is placed on their antiknock value. It is pointed out—and rightly—that this quality permits the use of high compression ratios and the attainment of higher efficiencies than would otherwise be possible. These high compression ratios will not be employed, however, until there is assurance that it will never be necessary to use fuels of less antiknock value whose performance in a high-compression engine would be extremely unsatisfactory.

France and Germany at least have given serious thought to the military side of availability. They have learned that motor vehicles should operate in time of peace upon fuels such that no changes in the induction system of the engine would be necessary to obtain satisfactory operation with the fuels available in time of war. As a result both countries have drawn up specifications for what they term "national fuels." The United States is not greatly dependent upon imports for its fuel supply. The question is frequently raised, however, as to how much the supply of motor benzene for fuel would be affected by the demand for toluene in the manufacture of explosives.

Usability

Usability is a matter of comparison. The question is not whether it is possible or impossible to use a certain fuel, but whether it is more or less difficult to use one fuel than another. For automotive work one must consider the difficulty involved: (1) in carrying safely an adequate supply of the fuel, (2) in preparing the fuel for combustion, (3) in distributing the fuel to the various cylinders, and (4) in burning the fuel in the time available. The supply of fuel that must be carried to travel a given distance is dependent upon the calorific value of the fuel. This is discussed later. Some of the other factors which affect the fuel's usability are—explosive range, distillation range, latent heat of evaporation, flash point, freezing point, separation point, viscosity, detonation characteristics, spontaneous ignition temperature, and corrosiveness.

The order of importance of these factors depends upon the type of service in which the fuel is used.

Explosion Range—This is defined usually as "the difference between the minimum and maximum volume that will explode when mixed with unit volume of air." Narrowing the explosion range increases the difficulty of engine operation. It often results in poorer fuel economy by preventing operation with mixtures as lean as could otherwise be used. Laboratory measurements of explosion range are not ordinarily directly applicable to engine conditions. In the engine, conditions of temperature, pressure, the degree of mixing, and the amount of inert gas present are different from those under which laboratory determinations are made. Nevertheless, it is highly probable that a fuel shown by laboratory tests to possess a greater explosion range than another will have a greater explosion range than the other when used in the engine.

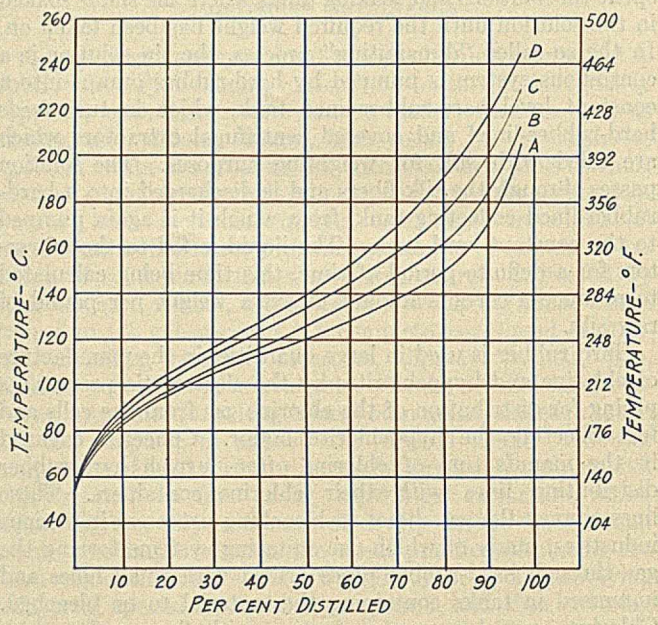

Fig. 1—Distillation Data on Fuels for Road Tests. Coöperative Fuel Research

Distillation Range—It is customary to show the distillation characteristics of a fuel by plotting temperature against per cent distilled. Typical curves for four fuels are shown in Fig. 1. Such curves are very informative as to the starting characteristics of the fuel and as to the probable ease of preparing it for combustion and distributing it to the

[1] Published by permission of the Acting Director, Bureau of Standards.

cylinders. The fuel in the charge must be mixed with the air if it is to be burned. The more finely divided the fuel the easier will become the task of thorough mixing. Vaporizing fuel is one of the simplest methods of obtaining fuel in this finely divided state. Moreover, fuel in the vapor form occupies many (in the case of gasoline about two hundred) times the volume it occupies when a liquid. For this reason vaporization is a material aid in the problem of mixing and distribution. The function of distillation curves is to indicate the relative amount of vaporization to be expected from different fuels at any given temperature. Starting characteristics of a fuel are dependent upon the temperatures at which the first 5 or 10 per cent is distilled. If this temperature is too high starting will be well-nigh impossible. The fuel-air ratio that must be furnished the engine for starting depends upon the amount of fuel that is vaporized under starting conditions. If only 5 per cent is vaporized the fuel content of the charge must be twice as great as when 10 per cent is vaporized. The objection to supplying this excess of fuel is not the cost of the fuel but the probable dilution of the oil by this excess fuel.

Perhaps a word as to the limitations of the distillation curve may not be amiss. It would be a mistake to determine from distillation data the temperature necessary for complete vaporization, and then, having determined that the charge entered the engine at a higher temperature, to conclude that the fuel must have been completely vaporized. The time required for vaporization must be considered and the size of the liquid drops as well as the temperature. With an engine operating at 3000 r. p. m. a complete cycle is completed in 0.04 sec. The Bureau of Standards, in coöperation with the American Petroleum Institute and the Society of Automotive Engineers, is now making tests to determine engine performance with the four fuels whose distillation characteristics are shown in Fig. 1. Interest in these tests centers about the fact that more than 30 per cent more D than A fuel can be produced per barrel of crude oil.

Under certain conditions a fuel may give trouble from being too volatile as well as from not being volatile enough. With a certain fuel altitude chamber tests of an engine were made impossible by the fact that the fuel vaporized in the fuel lines. This not only wrought havoc with the metering characteristics of the carbureter, but eventually stopped the flow of fuel entirely.

Extremely high volatility is, of course, undesirable because of the waste that takes place when the fuel is stored and because of the fire hazard.

Latent Heat of Evaporation—Vaporization is necessary. Vaporization in the time available requires heat. The higher the latent heat of evaporation the more heat must be supplied to secure a given degree of vaporization. Supplying heat is difficult. The greater the amount of heat to be supplied the greater is the difficulty. Hence, a low latent heat of evaporation is desirable.

Before leaving this subject it may be of interest to mention a condition occasionally found in aviation engine work. Some tests were being made at the Bureau when the engine performance suddenly became very erratic. The trouble was traced to the formation of a miniature snowstorm inside the intake system. Air containing considerable moisture entered the carburetor, its temperature was lowered because of the heat expended in vaporizing the fuel, and as a result water condensed and formed snow. This condition was remedied by supplying an additional amount of heat sufficient to vaporize the fuel.

Flash Point—In engine work this term is applied to the minimum mixture temperature at which ignition at one point will be propagated through the entire mixture. Ormandy[2] gives the following values of flash point:

	°C.
Gasoline	−25 to −30
Motor benzene	−11
95 per cent alcohol	16

The flash point in the engine would be somewhat different because of the influence of the pressure of the mixture at the time of ignition, the amount of inert gas present, the thoroughness of the mixing, etc. Nevertheless, the fact that, as measured, the flash point of alcohol was more than 40 degrees higher than that of gasoline would indicate that under some circumstances starting an engine would be more difficult with alcohol as a fuel than with gasoline. Such difficulty is reported from countries using alcohol fuel blends in automobiles.

Freezing Point—To define a desirable freezing point is easy: it is any temperature lower than the lowest ever reached in service. Most fuels are entirely satisfactory in this respect. Benzene is an exception, freezing at temperatures often encountered in winter in a considerable portion of this country as well as in flight. Fuel sold under the name "motor benzol" ordinarily contains sufficient toluene to lower the freezing point materially.

Separation Point—Many fuels are, and many probable fuels of the future will be, blends. There is usually some temperature, termed the "separation point," below which one constituent of the blend separates from the remainder. The usability of a blended fuel ceases when that fuel ceases to be a blend. Hence, one requirement of a blended fuel is that its separation point be at a lower temperature than is reached by the fuel in service.

Viscosity—This is included to call attention to the effect of changes in viscosity rather than to suggest any range of viscosities as being particularly desirable. The flow of fuel through the ordinary carburetor jet is considerably influenced by the viscosity of the fuel. In changing fuels, as for example from gasoline to alcohol with a viscosity twice as high, the proper jet size would be governed by the change in viscosity as well as by the change in fuel density and in the air-fuel ratio. Viscosity plays an important part in the change in mixture ratio resulting from a change in temperature. If an engine is operated on a cold day with the same carbureter adjustment as on a warm day there are two influences which tend to make the mixture leaner on the cold day. The weight of air received by the engine in unit time increases with decrease in temperature. Under these conditions the viscosity of the fuel increases and its flow decreases. Both influences are in the direction of leaner mixtures with colder air temperatures. The greater the change in viscosity with a given change in temperature the more sensitive will be the carbureter to such changes.

Detonation Characteristics—Detonation has received a great deal of attention during the past few years. Mr. Midgley has presented the results of some of his work before this Society. To the motor-car driver detonation often is known as spark knock. It causes the metallic ringing sound which results when a hill is climbed with the spark too far advanced or with the engine badly carbonized. This sound is accompanied by extremely high pressures which are often destructive to spark plugs and piston heads. Severe detonation usually results in a higher loss of heat to the jacket water and in a reduction of engine power.

Ricardo, in England, and Midgley, in the United States, have devoted a great deal of attention to the measurement of detonation, or the comparing of fuels on the basis of their detonation characteristics. Ricardo[3] has rated various fuels by means of what he terms "toluene values." He defines this value as "the tendency of a fuel to detonate in terms of its equivalent toluene content, taking standard aromatic gasoline as having zero toluene value and toluene as having a value

[2] *Automobile Engineer*, March, 1922.

[3] *Automotive Industries*, April 21, 1921.

of 100." In making determinations Ricardo used both a variable compression engine and a supercharging engine. In one instance he obtained a toluene value for one fuel of 28 by one method and of 18 by the other method. For another fuel the value determined by one method was 35 and by the other method 24. It would appear then that the toluene values as thus determined are not highly accurate, although useful as a basis of comparison.

Midgley[4] has measured detonation by what he calls the "bouncing-pin apparatus" and has published the results of tests of some blended motor fuels. He has rated the blends on an "equivalent xylidine in kerosene by volume per cent" basis. A table of the detonation characteristics of various blends of alcohol and kerosene follows:

Alcohol-Kerosene Blend		
Alcohol by Volume Per cent	Kerosene by Volume Per cent	Determined Equivalent Xylidine in Kerosene by Volume, Per cent
15	85	2.30
25	75	4.60
35	65	7.20
50	50	12.60

This table is given to call attention to one phase of the blended-fuel problem that at first glance seems inconsistent. If 2.30 parts of xylidine are equivalent to 15 parts of alcohol when blended with kerosene, it would not be unnatural to assume that $\frac{2.30}{15}$ (50) parts of xylidine would be necessary to give the equivalent antiknock characteristics of 50 parts of alcohol. $\frac{2.30}{15}$ (50) = 7.7, whereas the table shows 12.6 parts of xylidine to be necessary. A partial explanation lies in the fact that with the alcohol-kerosene blend when the knock-suppressing agent has increased from 15 to 50 parts the constituent whose knock is to be suppressed is only $\frac{50}{85}$ as great, namely, 59 per cent. With the xylidine-kerosene mixture the constituent whose knock is to be suppressed is $\frac{87.4}{97.7}$ as great, or 90 per cent. The problem is further complicated by the fact that the alcohol and xylidine differ in detonation characteristics as well as in their ability to suppress detonation. As far as this discussion is concerned it is sufficient merely to call attention to the fact that the relative amounts of two antiknock agents that are necessary to suppress detonation are not independent of the amount of either that is required.

High antiknock value is desirable even if the fuel is to be used in an engine which could be operated satisfactorily with a fuel of much lower antiknock value. Detonation increases with the accumulation of carbon. When the detonation reaches a certain degree of severity, the carbon must be removed from the engine. The higher the antiknock value of the fuel the greater can be the accumulation of carbon before the detonation will become so severe as to necessitate carbon removal. Hence, an increase in antiknock value makes engine overhaul less frequent.

Spontaneous-Ignition Temperature—The spontaneous-ignition temperature of a mixture of fuel and air is the temperature to which it must be raised in order to spontaneously ignite throughout its mass. Determinations of spontaneous-ignition temperatures are made in several ways, the results of which are not in as close agreement as might be desired. One method is to compress the air and fuel until they ignite from the heat of compression. Another method is to heat air and fuel separately and determine the temperature at which they will ignite upon being brought together. A third method is to let a single drop in the liquid state fall into a crucible heated to the required temperature and full of oxygen at that temperature.

A low spontaneous-ignition temperature is undesirable if the fuel is to be used in an engine operating on the Otto cycle, since it increases the liability of pre-ignition. Pre-ignition causes overheating and loss of power.

If the fuel is to be used in an engine of the Diesel type, a low spontaneous-ignition temperature is desirable. In such engines the scheme of operation is to compress air to such a temperature that the fuel will ignite when injected into it.

Corrosiveness—This property is among the undesirables. It may cause the failure of vital parts. It increases the wear of moving parts and consequently makes engine operation more noisy. How much corrosiveness should be permitted is dependent upon the class of service in which the fuel is to be used. Failure of a fuel line in an automobile means delay, in an airplane it may mean death. The presence of water or sulfur appears to be particularly undesirable from the standpoint of corrosion.

Power-Producing Ability

Fuel should have a high calorific value. Such a statement rolls easily from the tongue. If asked which is preferable, a high calorific value per unit weight of fuel, per unit volume of fuel, or per unit volume of combustible mixture, the answer may come more slowly. The calorific value of hydrogen per pound is nearly three times as great as that of gasoline. At 60° F. and atmospheric pressure hydrogen is a gas and gasoline a liquid. Under such conditions a cubic foot of gasoline has more than three thousand times the calorific value of hydrogen. A unit volume of combustible mixture has from 10 to 20 per cent higher calorific value when the fuel is gasoline than when it is hydrogen. Hydrogen is not suggested seriously as a fuel likely to be used extensively in internal-combustion engines. It serves to illustrate the difference between calorific value per unit weight, per unit volume, and per unit volume of combustible mixture. According to Ricardo, the total energy obtainable per unit volume of combustible mixture is the same within 3 per cent for hexane, heptane, benzene, toluene, xylene, and ethyl alcohol. The calorific power of these same fuels varies more than 60 per cent, considered on a basis of unit weight or unit volume.

It is probable that the calorific power per unit volume of combustible mixture is of most importance, since this determines the possible output of the engine per cycle. In all automotive work high calorific power per unit weight is desirable since a portion of the energy of the fuel must be expended in transporting the fuel, and high calorific power per unit volume is desirable because it permits the use of a small fuel container with a consequent low weight and wind resistance. These factors are most important in aviation work where the weight of fuel and tank is a much greater percentage of the total weight than in other branches of automotive work.

Calorific determinations tell how much energy is *in* a pound of fuel. It is more important to know how much energy can be obtained *from* a pound of fuel. Perhaps one may yet rate a fuel upon some such fantastic sounding basis as "obtainable foot-pounds per pound of fuel per proper engine." It is certain that the engine should be considered in conjunction with the fuel. At the Bureau of Standards aviation gasoline and motor benzene were operated in an engine having a compression ratio of 5.4. Both gave the same power. With aviation gasoline as a fuel satisfactory operation was not possible at a higher compression, but with the motor benzene the engine was operated at a compression ratio of 14:1 and an increase in power of 33 per cent was obtained with a corresponding decrease in specific fuel consumption.

[4] *J. Soc. Automotive Eng.*, June, 1922.

A discussion of this sort is apt to prove disappointing in that it fails to specify definite requirements. It states what is better and what is worse rather than what is right and what is wrong. It is hoped, however, that the discussion may have thrown some light on the various requirements of internal-combustion engines and their relative importance.

Economic Aspects of Motor-Fuel Supply from Petroleum[1]

By F. W. Lane and A. D. Bauer

Bureau of Mines, Washington, D. C.

IT IS EVIDENT to all who have to review chemical literature that there are periodic waves of interest in particular subjects, or in various aspects of these subjects. At one time there is a large number of articles on some one topic, whereas a few months later the center of interest has changed entirely. In no field is this more true than in the petroleum industry.

If we look back over the past fifteen years we find that there has been a steadily growing output of books and articles dealing with the economic aspects of this industry. At first these articles were largely descriptive, telling how the various products were made and used; then there began to appear a note of alarm—it was feared that the supply of crude oil was insufficient and that the demands made upon it would become too great. Of course, the war with its tremendous consumption of petroleum products intensified this alarmist literature and it continued to increase in size and importance up to the end of 1920. It seemed to be general throughout the petroleum industry, some of the ablest executives joining in the chorus. All of a sudden something happened. The price of crude oil dropped with a suddenness which shook the industry from top to bottom. As soon as the excitement caused by this sudden change subsided the industry tried to find out what really had occurred, and in the past two years a feeling has apparently grown up that our supplies of crude oil are inexhaustible, that all this alarmist literature was a mistake, that we are going to have sufficient oil for all our needs for an indefinite period. Within the past three months, however, the price of crude oil, at least east of the Rocky Mountains, has begun to rise again, and the increases have been so frequent that the industry is again trying to take stock of what has happened. It is not necessary to go into details of the actual production by fields, but the statistics of the past few months indicate the following things.

In the first place, California is producing a large excess of relatively high-grade oil, with the result that a considerable amount of California crude is being transported to the east coast by way of the Panama Canal for refining. In a way this seems to be providential, as this California crude is taking the place of the Mexican oil previously used, the past year having seen the beginning of a great decline of production in Mexico. Aside from California, however, the situation is not as hopeful as we might wish. There have been tremendous developments in Arkansas, but practically all the oil so far produced at Eldorado and Smackover is of the so-called "fuel-oil" grade. It is fairly high in sulfur and very little of it is used for the production of gasoline. On the other hand, the production in the Midcontinent district of the so-called "light crude"—that is, crude with a high gasoline content—seems at the present time to be very slowly declining.

Prophecy is impossible, however, at least in details. We may at any time find new fields of light crude which will more than make up for the probable decline of the present producing fields. If such fields are not developed, however, it looks as if economy in the use of gasoline and the development of possible substitutes will become more and more necessary.

History of Gasoline Industry

It was in the nineties of the last century that gasoline was first used as fuel for road vehicles. A few steam carriages were built in earlier years, but they were not very successful, and until the internal-combustion motor was developed and placed on rubber-tired wheels the self-propelled road vehicle was only an inventor's dream. The first successful automobiles used what was called "benzine" in those days, which was a by-product of the kerosene industry. This "benzine" or "gasoline," as it soon came to be called, was a good deal like the "fighting gasoline" furnished our aviators at the front, which was designed to give extra speed and power in airplane motors specially tuned up to its use. For several years the quality of gasoline remained about the same. Then it began to be apparent that the supply must be increased. More cars were being put on the road every day, and as the demand increased the refiners were forced to begin cutting deeper into the crude oil and putting more of it into the gasoline fraction. How far this process has gone is well known to every driver who remembers the gasoline of ten or twelve years ago. How much further it will go is a question on which some of our best technical men are working. It is doubtless true that we can use gasoline even less volatile than the present grades, but the steadily increasing demand for kerosene may make it necessary to stop raising the end-point of gasoline. In other words, there is an economic volume between the supply of straight run gasoline and kerosene.

The last ten years have seen other changes in the character of gasoline. The refiners found that they would have to make more motor fuel than could be recovered by ordinary distillation practice, and proceeded to do so by means of the so-called "cracking" processes. Gas oil, which lies between kerosene and lubricating oil in volatility, when heated under pressure will break down or "crack" to form gasoline. The early experimenters encountered difficulties such as too great a formation of fixed gases and carbon, which cut down the efficiency of the processes used and added to the expense of operation. Continued research, however, reduced these losses, and cracking is now being done at a profit. It is estimated that at least 20 per cent of our motor fuel is produced to-day in cracking stills.

About the same time that the refiners began to add to the size of the gasoline fraction, thus raising the end-point of the resulting motor fuel, the manufacture of natural-gas gasoline was started. This material is very volatile and is carried as vapor by natural gas, but it can be removed in the liquid state if the gas is highly compressed and then cooled. It has proved to be a valuable addition to our gasoline, as it furnishes a much needed supply of low-boiling hydrocarbons which are lacking in many grades of crude oil. While natural-gas gasoline amounts to only about 10 per cent of our total gasoline supply, it makes available as motor fuel a large amount of material that would otherwise be useful only as naphtha for solvent purposes. The older processes for making natural-gas gasoline depended on compression and refrigeration, but more recent ones have been developed in which the gas is passed through heavy oil or charcoal, which absorbs the gasoline. This is then recovered by distillation.

[1] Published by permission of the Director, Department of the Interior, Bureau of Mines.

Past Methods of Increasing Gasoline Supply

Therefore, the three principal methods that have been used in the last ten years to increase the supply of gasoline have been—first, raising the end-point; second, cracking gas and fuel oil; and third, making use of natural-gas gasoline. As already stated, it may not be possible to raise the end-point much higher, on account of the demand for kerosene. We cannot hope for a great increase in natural-gas gasoline, as the supply of natural gas is more likely to decrease than to increase as time goes on. The processes of cracking usually employed are limited by economic considerations. If the price of gas oil is low and the price of gasoline comparatively high, it pays the refiners to use cracking stills. There are, however, other large and important uses for gas oil, and its price therefore tends to rise until cracking ceases to be profitable.

Need for Further Increase of Motor-Fuel Supply

During the past several years our gasoline production has increased by leaps and bounds, as is shown by the following figures:

Production of Gasoline in Gallons

1904	291,000,000
1909	542,000,000
1914	1,467,000,000
1916	2,059,000,000
1917	2,850,000,000
1918	3,570,000,000
1919	3,958,000,000
1920	4,882,000,000
1921	5,154,000,000
1922	6,202,000,000

During December, 1922, the refineries produced more gasoline than ever before recorded, but in spite of this large increase in supply we have consumed the gasoline as fast as the industry has been able to produce it. Motor cars, trucks, and tractors are the main consumers of gasoline, and a glance at the production of automobiles and trucks indicates where our gasoline has gone.

Production of Automobiles and Trucks

1910	187,000
1915	892,618
1916	1,583,617
1917	1,868,947
1918	1,153,637
1919	1,974,016
1920	2,205,197
1921	1,668,550

Thus, it seems that our gasoline consumption is limited only by the amount available, for there is every indication of a continued increase in the output of internal-combustion motors, and it is readily apparent that we need continually increasing supplies of motor fuel.

Possible New Sources of Motor Fuel

Alcohol—Must we turn to the vegetable kingdom and depend on alcohol and similar fuels? Fortunately, it is not yet necessary to do so. Fortunately, because while the motor fuel that can be made from vegetable matter is replaceable—that is, while we can grow new crops each year that will yield alcohol—in most cases we can do so only at a tremendously increased cost. For example, the corn that can be grown on an average acre of Oklahoma soil in a year will yield about 3 bbls. of alcohol. Many of the oil fields of Oklahoma have an ultimate production of about 3500 bbls. of crude petroleum per acre, of which about 1000 bbls. can be considered as gasoline. One would have to grow corn on an acre of Oklahoma oil land for about three hundred years to obtain a volume of alcohol equal in fuel value to a supply of gasoline produced in from five to ten years. While these figures are limited in application and are not intended to discourage attempts to develop vegetable sources of motor fuel, they certainly show that it will be well first to investigate thoroughly our mineral resources.

Coal—Although crude petroleum is paramount in importance, there are several other mineral sources of motor fuel. Of these, the most valuable to-day is coal, from which we obtain benzene. Commercial benzene is a mixture of volatile hydrocarbons and is made as a by-product of the coke industry, either by distilling coal tar, or by passing coal gas through absorbing towers. It is a good motor fuel when used alone, and has especial value when mixed with gasoline as it tends to prevent detonation. It must, however, be properly refined. When benzene was first used in this country as a motor fuel the excess of sulfur contained in it caused corrosion of the needle valves and other exposed parts of the carburetors. The manufacturers have learned how to remove this dangerous excess of sulfur, and most benzene of to-day is free from this fault. The supply, however, is limited. It has been estimated that the maximum development of the coal-tar industry possible in ten years will increase the production of benzene to 350,000,000 gal. per year, which is only about 6 per cent of our present motor-fuel requirements.

Oil Shale—While coal is the one mineral, aside from petroleum, from which we are getting motor fuel at present, it may be of less ultimate importance in this regard than oil shale. Much has been written about the vast deposits of shale, particularly in the West, and there seems to be little question but that eventually there will be a great and flourishing industry founded on this mineral. It has been estimated that there are locked up in the shale beds stores of oil many times as large as the total recoverable oil in the sands. But at the present time the shale-oil industry is in the experimental stage, and we are still in the process of acquiring the fundamental knowledge and technic necessary to enable us to make high-grade oil on a commercial scale. The manufacture of oil from shale has been carried on for years in Scotland, but the American shales are somewhat different in character, so that the Scotch methods are probably not applicable in this country unless modified. The mainstay of the Scotch shale industry is the yield of ammonia, and the oil is more or less a by-product. American shales do not yield much ammonia, and the industry will, therefore, have to make oil its main product, thus coming into direct competition with petroleum products. Accordingly, for a long time to come, the price obtainable for shale oil will be set by the prevailing prices for crude petroleum, and the best authorities agree that even though shale may eventually furnish most of our motor fuel, at the present time it is only in favored localities and under the most careful management that a shale-development company can succeed.

Possibilities in Vegetable Kingdom—If, then, the resources of the mineral kingdom outside of the field of crude petroleum are limited, either in quantity or on account of our present lack of knowledge or by economic conditions, what do we find on investigating the vegetable kingdom? One outstanding fact—that most vegetable products already have important uses, and the only materials that can be economically used for the production of motor fuels are the vegetable wastes of to-day, or are plants that can be grown on land that is not now needed for other purposes. As already stated, it would take three hundred years to grow enough corn in the oil fields of Oklahoma to obtain a volume of alcohol equivalent to the production of gasoline obtainable in a few years. Of course, the area of the oil fields in the country is but a small part of the total area of the United States, but this simply emphasizes the fact that while we can grow corn over an area many times as large as the area of the producing oil lands, it will then have to be harvested

and brought to the distilleries, a laborious and expensive task. Furthermore, edible grain of any kind is usually too valuable to be used for the manufacture of alcohol. And even if we had a surplus it would be a mere drop in the bucket. A surplus of 1,000,000,000 bu. of corn would sound tremendous to the farmers of this country, but it would yield only 250,000,000 gal. of motor fuel, enough to run our cars and trucks about three weeks. The same reasoning applies to all other sound grains, vegetables, and fruits. At present they are too valuable as food for man or for stock feed to be used to make motor fuel, and if there were a surplus available it would be too small to be of much importance in the aggregate supply.

The case is somewhat different with waste products. According to the records of the Department of Agriculture, this country produced 286,085,463 gal. of alcohol, mostly from waste molasses, during the fiscal year ending June 30, 1917, when production was stimulated to its highest point. The other large source of vegetable waste is the lumber industry. Although a good deal of experimenting has been done, little alcohol has been produced from wood waste, as the process is rather complicated, and also because the yield is small compared to the yield from molasses. The Forest Products Laboratory estimates, however, that there is enough wood waste available every year in this country to produce 240,000,000 gal. of alcohol. It is variously estimated that this country could, if necessary, produce from 500,000,000 to 1,000,000,000 gal. of alcohol, or from 8 to 16 per cent of our present motor-fuel needs.

Most Hopeful Methods of Providing for Future Needs

But the most important aspects of the motor-fuel problem have still to be discussed. Liquid fuel obtained from coal and lignite is good as far as it goes, but the supply is small as it is a by-product, and its production depends on the utilization of the coke produced at the same time; shale oil is of great future but little immediate value; alcohol from vegetable sources will always be limited in quantity, and cannot be produced to-day at a price to seriously compete with gasoline. The three methods that the refiners have employed up to the present time to get more gasoline have been shown to be inadequate to provide for all our future needs, but there are other methods available to the petroleum industry which seem to offer great hopes for the future.

One method is to use gas oil directly as motor fuel. Cracking involves a loss of material and requires the consumption of fuel. For instance, if we crack gas oil we lose part of the total heating value of the oil and in addition consume other fuel in the cracking distillation. Obviously, if the gas oil can be used in an internal-combustion engine, we save these losses. It is gratifying to see that work is actively progressing in developing automotive engines to use heavy oils.

Another method is to discover new oil fields. If we could be sure of finding a new Cushing or a new Burbank field every year or two, we would not have to worry at all about substitutes for gasoline. Unfortunately, this is not as easy to do as it is to recommend, but as long as new production is found as fast as it is needed all will be well. But even to-day we are importing part of our oil, and we probably will continue to do so in larger and larger amounts. Undoubtedly, the undeveloped areas of the world contain large oil fields, but other nations are awake to the need of oil and only a part of these resources will be available for us.

But there are other ways in which production can be increased. Wells that have been abandoned are to-day being repaired and are again producing oil in paying quantities. Large-scale experiments have shown that whole properties can be reworked with modern methods, and in some cases in Ohio, Pennsylvania, and West Virginia as much oil has been recovered as was done before the properties were considered ready for abandonment.

Furthermore, after the oil is above ground a great deal can be done to conserve it. A recent investigation of the Bureau of Mines disclosed large losses of oil by evaporation between the well and the refinery. The material that was lost was principally the best portion of the gasoline contained in the crude, and if saved, as much of it can be by proper methods of handling, it would add materially to the quantity and value of our gasoline. Similar losses occur in many phases of the transportation and refining of crude oil and gasoline, and the aggregate preventable loss is enormous.

If, then, the producer and refiner of oil have it in their power to increase the amount of gasoline, and if this can be added to by other sources, as already shown, will there be enough motor fuel for our future needs? There will be if the automotive engineers, and especially if the public that drives cars, coöperate. It is gratifying to see the great interest that has developed recently in conservation and efficient utilization of all petroleum products, especially of gasoline. The public is becoming aware of the folly of using rich mixtures, and of running with one cylinder missing. Steps are being taken by the associations of oil refiners and automotive engineers to get together in a spirit of coöperation and mutual assistance, and solve some of the larger problems involved. These leaders in the petroleum and automotive industries realize that, while there may be supplemental fuels, still it is to petroleum that we must look for our motor-fuel supply, and the possibility of furnishing this needed motor fuel rests upon the producers and refiners of crude oil, who must seek increased production. But at the same time all must practice conservation to the utmost in order to utilize effectively all of this precious resource that we now have.

Use of the Bunsen Valve in Connection with a Filter Pump[1]

By Fred W. Ashton

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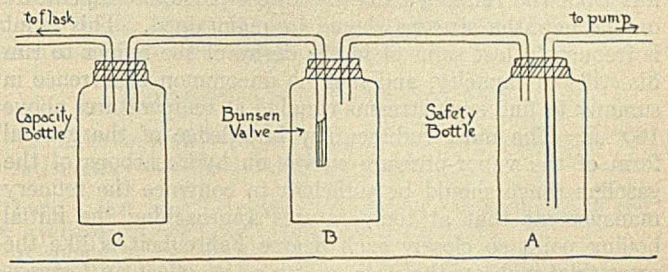
During the course of some recent work, the author was using "vacuum" subject to considerable fluctuation, due both to variation in water pressure and to variable "pull" by another worker. The annoyance and difficulties caused by these variations were successfully overcome by the use of the Bunsen valve.



A is the regulation safety bottle used to prevent the backing up of water from the pump. B is the bottle for the Bunsen valve. C is an extra 2.5-liter bottle for "capacity." The valve is placed on the tube leading to this bottle. With this arrangement a fairly high vacuum can be maintained in the flask, even with almost complete momentary stoppage of the pump or temporary opening of the line on the pump side of the valve.

[1] Received April 11, 1923.

Refinery Problems Affecting Motor-Fuel Supplies

By F. A. Howard and N. E. Loomis

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IN PRESENTING this paper it is not the intention of the authors to describe any new equipment or to present original data, but rather to summarize facts which are well known to petroleum technologists but which are too often neglected in refinery operation. Further, since this paper deals solely with present refinery problems, the many interesting technical questions involved in the possible use of shale oil, alcohol, benzene, etc., will not be discussed.

As was pointed out by one of the authors in a paper presented before the American Petroleum Institute in 1921,[1] the most important single problem affecting motor fuel supplies at the present time is that of the production and conservation of a maximum quantity of the highly volatile fractions of gasoline. Gasoline specifications require a certain ratio of light to middle to heavy fractions, and no matter how much the quantity of middle or heavy fractions may be increased, the supply of motor fuel will be limited by the supply of light fractions, unless a sacrifice of volatility is permitted. The problem of supplying these light fractions becomes of increasing importance from year to year.

As far as the refiner is concerned, cracking offers the only means of directly increasing the production of these light fractions, and that its important function in this connection is well recognized is proved by the widespread interest which now exists in regard to such processes.

Less attention has been paid, however, to the equally important phase of conserving these highly volatile fractions. The very nature of these fractions results in the losses incident to refinery operations being largely at their expense. Their conservation may be considered from these angles—(1) proper processing equipment and methods, (2) recovery of volatile liquid hydrocarbons from refinery gases, and (3) protection against evaporation losses in storage.

Proper Processing Equipment and Methods

The use of ample condenser surface and proper arrangements to provide countercurrent flow between the cooling water and the oil is essential on all distillation equipment with low-boiling stocks. The amount of gasoline carried off by the gas from such stills increases rapidly with increase in temperature, and to prevent this loss and subsequent loss from the running pans the lowest possible temperature on the naphtha streams should be maintained. This point is frequently lost sight of in the desire of the refiner to run his stills to capacity, and it is no uncommon occurrence in summer to find such streams running at temperatures above 100° F. The most rudimentary knowledge of the general form of the vapor-pressure curves on hydrocarbons of the gasoline range should be sufficient to convince the refinery management that at temperatures approaching the initial boiling point so closely each degree Fahrenheit is like the proverbial inch on the nose, as far as its effect on losses is concerned. Nevertheless, it is sometimes difficult for the refinery chemist or engineer to make the full importance of this clear, and as a result preventable losses of light gasoline are still more common than they should be.

The "look-boxes" of the stillhouse should be gas-tight and should be connected into the refinery gas system. A gas exhauster on the gas-collecting system should maintain as nearly as possible a balanced pressure on these boxes. Care should be taken not to draw air into the gas lines, for this greatly reduces the efficiency of any gasoline-recovery system.

The "running pans" into which the distillate streams flow provide another common source of loss. In these pans the naphtha is being continually agitated by the constant inflow and intermittent pumping. When the pans are equipped with loose hatches, a stream of gasoline vapors frequently can be observed pouring out. The naphtha pans should be equipped with tight roofs and connected into the gas-collecting system. Further loss from the pans is frequently caused by carelessness in drawing water off the bottoms, allowing some of the oil to run to the sewers.

From the pans the subsequent handling of the naphtha should be in gas-tight equipment. The use of open agitators for treating and sweetening, which permit the escape of vapors, is unnecessary and wasteful.

Recovery of Volatile Liquid Hydrocarbons from Refinery Gases

In the preceding discussions it has been assumed that the refinery is equipped with a gas-collecting system. Many refiners still neglect this, and even insist that the amount of gas produced in ordinary distillation is negligible. This may be true in rare instances, but in general the value of the gas and the gasoline that can be recovered from the gas makes a proper collecting and gasoline recovery system a good investment. The amount of the gas which must be handled may be materially reduced by attention to the points already made—exclusion of air and maintenance of low temperature on the naphtha streams.

There are many modifications of gasoline-recovery systems. It is difficult to decide to just what extent recovery is justified. By using a high-pressure process, gross recoveries can be materially increased over what is possible at atmospheric pressure, but this increased recovery is chiefly in the least stable fractions. The decision in regard to the type of system to be used must be based upon a comparison of costs with amount of gasoline that can be put into the purchasers' hands, and this item is dependent upon such factors as amount of blending stock available, time spent in storage before marketing, weather conditions, etc. It is a fact, however, that any system is so much better than no system at all that consideration of relative merits of different processes should not be permitted to delay action very long.

Protection against Evaporation Losses in Storage

Probably the greatest single source of loss of gasoline at refineries is evaporation from storage tanks. On finished products this loss is especially serious, in that not only the material, but the cost of refining it is lost.

Here again the loss is predominantly at the expense of the most volatile fractions. Tests carried out at various refineries have shown that the average gasoline in standard steel tankage will lose about 6 per cent per year, equivalent to over $30,000 for each 55,000-bbl. tank. The magnitude of these evaporation losses has caused much work to be done on means for decreasing them. The common suggestions made in the past may be grouped as:

1—Means for keeping the contents of the tanks cool—such as spraying, insulation or jacketing of sides and roof, special paints, etc.

2—Means for preventing diffusion and drafts—such as special breather valves, protection of eaves from leaks, etc.

[1] Howard, "Qualitative Limitations in Refining and Marketing of Gasoline."

3—Means for eliminating breathing losses and recovering gases delivered from tanks—such as tight-roof tanks connected to gasometers and gasoline-recovery systems.

There are merits to most of these suggestions, and most of them will repay their use under favorable conditions; but none of them has appeared to be a generally adaptable solution of the problem, either because it affected only one cause of the loss or because of undue expense.

For this reason the Development Department of the Standard Oil Company (N. J.) began work about three years ago to find a universally satisfactory solution of the evaporation problem. The basis of this work was the idea that the surest preventive was to float upon the surface of the oil some fluid which of itself had a negligible vapor pressure. Unfortunately, Nature has so ordered things that all light liquids have high vapor pressures. The problem, therefore, resolved itself into the production of a liquid of low vapor pressure and insoluble in gasoline, with which could then be incorporated other material sufficiently light to float the mixture. To make a long story short, this eventually led to the development of the product known by the trade name of "Sealite," which is essentially a mixture of glucose, cornstarch, glycerol, glue, and calcium chloride, so proportioned that it is insoluble in oil, incombustible, nondrying, does not absorb moisture, and does not ferment. The original solution can be readily pumped and handled in tank cars. It weighs, however, about 11 lbs. per gal., and in this form will, of course, not float upon oil. The finished "Sealite" is made by beating the "Sealite" solution with air to produce an emulsion or foam. This beating must be carefully controlled to give a product weighing about 4.75 lbs. per gal. The inclusion of too little air will not make it light enough to float on gasoline, and the inclusion of too much air makes it so stiff that it will not flow properly upon the surface of the oil. Microscopic examination indicates that the air bubbles are 0.0005 in. in diameter. This foam is handled in barrels and applied to the surface of the oil in the storage tanks. Tests have shown that a 1-in. layer of it will last at least a year, and in that time will reduce the storage loss to at least one-fifth of normal loss. In fact, the prevention of evaporation is practically complete and the observed losses are probably mainly due to leakage and escape of permanent gas. The material is entirely soluble in water, and, although this is an advantage in the cleaning of tanks, it necessitates weather-tight tank roofs.

In addition to minimizing evaporation, "Sealite" is an effective fire-prevention agent. Tests carried out on small tanks have shown that when the layer of "Sealite" is broken and the oil ignited, the foam will quickly flow together again and extinguish the blaze. This occurs even if the "Sealite" and oil are first subjected to violent disturbance. In these tests the "Sealite" has not been destroyed, but is only charred on the surface, and the fire test can be repeated several times with the same lot of foam. We believe that in the case of large tanks covered with "Sealite," even if the break in the protective blanket is so extensive as to prevent its closing entirely, the fire will be localized to a small portion of the surface and will, therefore, be much easier of control.

"Sealite" passed out of the experimental stage last year, and is now being used by several large companies on both gasoline and crude storage. Up to the present time a total of over 14,000,000 bbls. of gasoline and light crude oil have been protected in this manner. The effectiveness of the protection afforded leads us to believe that "Sealite" constitutes a definite advance in efforts to conserve the light fractions of petroleum and thereby increase the quantity and better the quality of our available supplies of motor fuel.

Alcohol as a Motor-Fuel Constituent[1]

By Henry A. Gardner

For the Bureau of Aeronautics, Navy Department, Washington, D. C.

GASOLINE, even of the highest grade aviation type, is not entirely satisfactory as a motor fuel, at least for aircraft. Impurities present have caused corrosion difficulties. Detonation troubles have been serious. It has not been economical because it cannot be used effectively at high compressions, as such compressions—say 7:1—are obtainable from a practical standpoint only when detonation can be prevented.

Benzene-gasoline mixtures have been used for a considerable period of time to prevent detonation, and in this respect have probably been satisfactory. Ordinary motor benzene, however, may be rich in gum-forming agents and of high sulfur content, so that considerable corrosion difficulties are possible. A very high-grade benzene, free from such products, is apparently difficult to obtain in large quantities, on account of the already existing market for the ordinary grades for use in making automobile-gasoline blends. Moreover, the production of benzene is not unlimited, and the requirements in war time for explosive purposes might be so great as to cause interference with its use as a fuel. Furthermore, it has a tendency to cloud at low temperatures, and partial solidification within fuel lines might be caused at very high altitudes. The percentages of benzene necessary with compression ratios greater than 6:1, for instance, would be dangerous, from this standpoint, at high altitudes.

Other "antiknocks" have been proposed for use with gasoline, and various metallic ethyl compounds have been experimented with in this direction, excellent work having been accomplished by certain research workers in this field. It has been stated, however, that the effect upon spark plugs in high-compression engines would make its use for aeronautics inadvisable at present.

Alcohol has been experimented with for a considerable period of time, being mixed with gasoline in various proportions, usually 95 per cent alcohol being used. Ether, benzene, and other materials have been added to the mixtures to effect miscibility and prevent separation. Corrosion troubles due to the water present, the impurities in the benzene or gasoline used, separation of constituents, and the bad odor of the ether, have sometimes been observed with such mixtures, and they have not therefore been found generally satisfactory.

Absolute alcohol has recently been made in large commercial quantities, and offers considerable possibilities as a constituent of motor fuels, being miscible at all temperatures and in all proportions with gasoline.

Requirements for Aircraft Fuel

It might be well to outline in general the requirements for a satisfactory fuel for aviation purposes:

Such a fuel must be made in large commercial amounts and be available in practically unlimited quantities.

It should be low in cost.

It should be practically free from gum-forming constituents or corrosive agents, so that it will not attack or plug up valves or affect the interiors of combustion chambers.

[1] The Bureau of Aeronautics of the U. S. Navy has been experimenting for a considerable period of time on blended fuels for aircraft. Some preliminary observations made available to the writer through his association with the bureau in this work have been summarized in a general way. No final conclusions are being drawn from the work conducted to date—which is, of course, of a preliminary nature—this presentation being merely descriptive of the type of experiments now being carried on by the bureau.

It must be of an antiknock character, so as to prevent detonation.

It must be sufficiently high in thermal value.

It must be of such a nature as to allow handling without separation, when used with gasoline.

Its use as a fuel should not interfere with war-time requirements for other important purposes.

Possibilities of Alcohol-Gasoline Mixture

In the writer's belief, absolute alcohol-gasoline mixtures will answer most of these requirements, and it is suggested that mixtures containing 30 per cent absolute alcohol and 70 per cent gasoline be experimented with for this purpose. Experiments so far would indicate that although absolute alcohol has a lower British thermal unit per pound than benzene, it has a greater antiknock value. It has also been indicated that a pound of alcohol 30–gasoline 70 mixture has practically the same calorific value as a pound of a similar mixture of benzene and gasoline of equal antiknock value.

Aside from the advantage of using such an alcohol-gasoline mixture to cut down detonation, comes the possibility of making a product that will reduce corrosion difficulties. For this purpose, however, it is suggested that the type of gasoline used in such a blend should be refined by some material such as a mineral gel, in order to remove impurities. After treatment, the gasoline should substantially meet the following specifications:

Not darker than 25 Saybolt color.

Freedom from mineral acids.

Negative doctor test.

Negative copper-strip test.

When 100 cc. are evaporated in a copper dish, not more than a slight fluorescence shall be shown, and the residue shall not be over 0.015 g.

It is possible that instead of using high-grade aviation gas as a basis for the refined gas, cheaper grades of the correct distillation values could be used, provided the gas is refined to meet the above requirements. Gasoline prepared from highly saturated petroleum will be found best. It will also aid in preventing the separation of the alcohol should small amounts of water be absorbed.

It is also advisable that specifications be observed for the type of absolute alcohol used. Alcohol for this purpose should be of as high a strength as it is possible to obtain commercially. It should be practically free from aldehydes or other gum-forming agents. The acidity of 100 cc., expressed as acetic acid, should not be over 0.01 g. When 100 cc. are evaporated in a copper dish, not over 0.006 g. of residue should be left, and no discoloration of the metal should be observed. It should be miscible with gasoline in all proportions, and not cloud at any temperature encountered at high altitudes.

It is probable that a mixture made up with the foregoing materials will reduce carbon formation to a very great extent, eliminate detonation troubles, cause smoother operation, and give longer life between overhauls to motors.

Shipment

The question of shipment of such alcohol to various stations is one, of course, that must be considered. It is probable, however, that special permits could be obtained, at least for government users, under Formula 28A of the Bureau of Internal Revenue, which it is understood calls for 1 gal. aviation gas admixed with 100 gal. alcohol of at least 198 proof. Such a type of alcohol is not potable even upon distillation, the gasoline carrying over with the alcohol and giving it a very disagreeable taste and effect.

Prevention of Corrosion

Referring back to the subject of corrosion, it should be understood that considerable trouble has been observed in gasoline tanks. These were at first made of copper. They became clogged with scale. The presence of small amounts of acid used in refining the gasoline, or of sulfur, was probably responsible for this effect. The sulfur also had a very bad effect upon carburetors. Later terne plate was used, and considerable corrosion was observed, probably due to the same causes. Later aluminium tanks were developed, and these were found, as a general rule, quite satisfactory except where water was present in the gasoline. The water upon settling out at the bottom would cause rather rapid corrosion, aluminium hydrate being formed, which would be carried up into the carburetor bowls as a slimy white mass. Where the flux from the soldering material used in constructing these tanks was thoroughly washed out previous to using the tanks, and gasoline free from water was used, very little difficulty was presented. The use of baked japan coatings as liners might also be considered or the daily tapping of the tank bottoms through suitable outlets.

Points under Investigation

Tests are under way now, on a rather large scale, with a fuel of the 30 alcohol–70 gasoline type, several thousand gallons having been prepared for navy experiments. Some of the points that will be very carefully observed during this investigation will be as follows: methods of blending, separation tendencies, effect on power output of engines, comparative ease or difficulty of starting engines, increase or decrease in amount of sediment in fuel-line strainers, difference in smoothness of operation, comparative life of spark plugs, effect on temperature of oil and water, life of engines between overhauls, decrease or increase of valve leakages, effect upon water-jacket failures, decrease or increase in forced landings due to engine failures, comparative carbon deposits in engines, comparative stoppage of carburetor jets, and comparative amounts of foreign matter in carburetor bowls, effect upon piston-head corrosion or sticking of piston rings, effect upon power-plant operation, and conditions observed during operation at very high altitudes.

Another point worthy of consideration is the development of methods of preventing absorption of water. A fuel of the 30 absolute alcohol–70 gasoline type, when left outside in an uncovered container, exposed to a damp atmosphere for about 10 hrs., will absorb sufficient water to cause separation of the two constituents. When kept inside the laboratory during that period of time, separation does not occur. When placed in covered containers having about two-thirds air space, allowing a small hole in the container cover as a vent, placement outside for a period of three days in very damp, cold weather apparently does not cause separation. Tests conducted with the addition of small increments of acetone, benzene, and other ingredients to help maintain the equilibrium of the mixture do not indicate any great success. It is possible, however, that certain materials may be developed which will be satisfactory in this regard. Many products that act as blending agents have corrosive tendencies, and are therefore to be avoided.

Corrosion tests made on various types of metal with the 30–70 type of fuel so far have indicated no stimulation of corrosion, because of the very high degree of purity of the product and absence of rust-stimulative compounds. Tests also show an extremely low cloud point, lower probably than would ever be obtained in actual service. For instance, mixtures of 30 absolute alcohol and 70 gasoline will show cloud points of from −46° to −60° C., depending upon the type

of gasoline used. The addition of water to such mixtures, even in small amounts, will rapidly raise the cloud point, the presence of 0.5 per cent water generally causing the mixture to show a cloud point in the neighborhood of −10° C.

The possible use of calcium carbide for dehydrating alcohol and the consequent carburetion of the product with acetylene affords further material for study. Alcohol so prepared as a fuel possibility is well worthy of investigation.

Coal Tar as a Source of Fuel for Internal-Combustion Engines

By Wilbert J. Huff

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In 1920 this country produced about 120,000,000 gal. of crude light oil from coal-gas and coke-oven plants.[1] If all of this were converted to motor fuel, it would be sufficient to give over 1,700,000,000 Ford miles, assuming an 80 per cent yield on refining and 18 miles per gal.; yet, this quantity of crude light oil is equivalent to only a little more than 2 per cent by volume of the gasoline produced in this country at the same time.

Although the lighter oil products from the carbonization of coal thus constitute a very small fraction of the total fuel available for internal-combustion engines of the explosion type, they nevertheless stand high in the esteem of the purchaser chiefly because of their combustion characteristics, for these oils, when blended with gasoline, enable the operator to advance the spark and open the throttle, and thus attain higher compressions, and so higher efficiencies, without inducing detonation.

Light oil from the carbonization of coal consists chiefly of benzene and its homologs, and such are classified as coal-tar derivatives. However, practically all the coal tar produced in this country contains so small a quantity of these that in normal times coal tar is never treated for its light-oil content, and all of the light oil produced in this country comes from another source, gas scrubbing.

This paper, therefore, will not consider these materials except to point out in passing that the combustion characteristics which render them so desirable to the operator of the explosion motor when encountered by analogy in the heavier products of carbonization in driving burning motors of the Diesel type, not only do not offer an advantage, but even present a disadvantage.

Nature of Coal Tar

Dehydrated coal tar from high-temperature carbonization is a complex mixture consisting chiefly of a great number of hydrocarbons of the aromatic type, together with a small percentage of oxygen-containing compounds largely of the phenol type, a small percentage of nitrogenous materials chiefly of the pyridine type, a small percentage of aromatic sulfur compounds, and a varying percentage of an important, but little understood, ingredient composed chiefly of carbon and generally designated as "free carbon." In addition to these normal constituents, coal tar may contain a small amount of mineral matter or ash-forming material, probably finely divided coal or coke dust carried mechanically from the retort by the gas stream.

Such a dehydrated high-temperature coal tar shows very little distillate at vapor temperatures below 160° C. When the vapor temperature attains 350° C. a very considerable residue remains in the still. This will usually be more than 50 per cent of the original charge and may be more than 70 per cent, and is the familiar bituminous aggregate known as coal-tar pitch. Such tar, then, does not offer much promise as a fuel for engines of the automobile type, nor indeed for any type, without some preliminary refining.

Solid Distillation Products—Naphthalene

When refined by distillation, coal tar may be the source of two fuels for internal-combustion engines, a liquid and solid. When cooled, the bulk of the distillate is liquid, and this liquid has been extensively utilized in Europe as a fuel for Diesel engines. The solid deposited by the first fractions (below a vapor temperature of 270° C.) is chiefly crystalline naphthalene. This may be centrifuged and recrystallized, giving, by a very simple process, a hydrocarbon sufficiently pure to serve as a fuel for internal-combustion engines. A patent on this use was granted to Chenier and Lion.[2] Naphthalene has been used successfully as a substitute for gasoline in the propulsion of motor cars. The boiling point of naphthalene (218° C.) lies within or close to the boiling-point range of much of the gasoline sold in the United States. According to Gad[3] a large auto bus driven by finely powdered naphthalene ran regularly between Paris and Versailles. To drive such motors thus requires some modification of the ordinary feeding and carbureting mechanism.

Most motors feed the naphthalene in liquid form, and are consequently obliged to start and run for a short time on gasoline or other light oil until the cooling water or the exhaust gas line has attained sufficient temperature to melt the naphthalene and to preheat this and the inlet air to a temperature sufficiently high to insure flexible control. The gasoline supply is then discontinued.

The literature records so many favorable reports[4] of the use of naphthalene for automobile, marine, and small stationary engines, that such use may be said to be established. According to Venton-DuClaux, prior to 1913 naphthalene was adopted as a fuel by the Trans-Siberian Railway. Comparative trials on motor cars in Paris indicated a fuel consumption of only about 3.4 lbs. of naphthalene when substituted for 1 gal. of petroleum spirit.[5] According to an anonymous communication to the *Gas World*[6] an 8 horsepower engine will consume $^3/_4$ lb. per horsepower-hour at full load, and 1.1 lbs. at 3.2 horsepower. The average consumption for larger engines has been taken as 300 g. (about $^2/_3$ lb.) per horsepower-hour.[7] The thermal value of naphthalene is approximately 17,300 B. t. u. per lb., or 9600 Cal. per kg.

Naphthalene is obtained not only by direct distillation of the tar from high-temperature carbonization, but also by further condensation from the gas after it has been freed from tar, the tar having, however, carried out with it most of the naphthalene derived from the carbonization of the coal. This further condensation of naphthalene from the gas occurs chiefly at the final coolers of the coke-oven by-product plant. Tests at the plant of the Seaboard By-

[1] McBride, "Manufactured Gas and By-products, Mineral Resources of the United States," Part II, 1920, p. 440.

[2] Ger. Patent 144,942; Lunge, "Coal Tar and Ammonia," **1916**, p. 848.

[3] *Oesterr. Chem. Tech. Ztg.*, **27** (1919), 48; *C. A.*, **3** (1909), 1680.

[4] Heller, *Z. Ver. deut. Ing.*, **58**, 21; *C. A.*, **8** (1914), 2613. Anon., *Petroleum Rev.*, **28** (1913), 672; *C. A.*, **7** (1913), 3223. Anon., *Gas World*, **58** (1913), 2; *C. A.*, **7** (1913), 887. Venton-Du Claux, *Gas World*, **58** (1913), 82; *C. A.*, **7** (1913), 1282. Schröder, Ger. Patent 291,507, March 8, 1912; *C. A.*, **11** (1917), 884. Willis, *Gas J.*, **141** (1918), 65; *C. A.*, **12** (1918), 860. Lunge, *Loc. cit*, p. 848, gives additional references.

[5] Lunge, *Loc. cit.*, 6 kg. of naphthalene were equivalent to 14.7 liters of petroleum spirit. This seems to be a very high efficiency for naphthalene.

[6] *Gas World*, **58** (1913), 2.

[7] *France-Belgique*, **2** (1922), 36; *C. A.*, **17** (1923), 458.

Product Coke Company have indicated that the naphthalene deposited here amounts to approximately $^1/_2$ lb. of naphthalene per ton of coal carbonized. This is sufficient naphthalene to move, in 2-ton motor trucks, the coke produced a distance of about $1^1/_3$ miles and return the trucks to the starting point, assuming a coke yield of 75 per cent, a fuel consumption of 7 miles per gal. of gasoline, and a naphthalene-gasoline ratio equivalent to that reported by Lunge. If to this naphthalene were added the naphthalene which could be recovered from the tar,[8] there would be sufficient to move the coke over $5^1/_2$ miles farther and return the trucks. Since transportation conditions are usually such that only a fraction of the coke need be handled by truck, it appears that sufficient naphthalene is available to supply an important fraction of the motor-fuel needs of the carbonizing plant.

In this country many plants do not even attempt to recover the naphthalene from the final coolers. Thus, the total production of crude and refined naphthalene from coke-oven operation in the United States for 1921 was but 2,942,985 lbs. on a total of 28,813,111 tons of coal charged,[9] or only approximately 20 per cent of the naphthalene deposited at the final coolers, or approximately 4 per cent of the total naphthalene available from carbonizing operations in by-product coke plants. This low production may be attributed to the fact that the possibilities of naphthalene as a high-grade fuel have not been properly exploited here.

However, naphthalene in mixture with gasoline has been used to some extent. Certain "secret" preparations, which (according to the venders) endow gasoline with remarkable properties when added in the proportion of 1 tablespoonful of the "secret" to 5 gal. of gasoline, consist chiefly of naphthalene to which some color or perfume has been added as a mask. While the properties of such a gasoline-naphthalene mixture have no doubt been unduly exaggerated by the venders, it appears that the addition of naphthalene to gasoline may form a mixture possessing certain advantages. The naphthalene gives a mixture of higher viscosity,[10] and so, in general, for the same carburetor setting such a mixture should give a greater mileage. In addition, the naphthalene is said to serve as an antiknock material, thus permitting the use of higher compressions. Mixtures of naphthalene and petroleum products are, however, limited by the comparatively high freezing points of such solutions with only low concentrations of naphthalene. Naphthalene is in general more soluble in aromatic hydrocarbons, so it would appear that some naphthalene could be profitably added to motor fuel composed of benzene-gasoline blends.

Beyond the naphthalene-containing fractions—i. e., above approximately 270° C.—the solids obtained by the cooling of high-temperature coal-tar distillates are designated as crude anthracene, which consists of anthracene, phenanthrene, carbazol, and a great many other compounds of related constitution, many of which have never been identified. So far, these mixtures of anthracene and similar solids do not appear to have been utilized as fuel for internal-combustion engines.

Liquid Oils

The liquid oils obtained after the naphthalene and anthracene are removed possess in general so low a vapor pressure that they cannot be used by the ordinary explosion-type internal-combustion engine, and the combustion characteristics are such that for a long time attempts to use such oils in motors of the burning or Diesel type were unsuccessful.[11]

[8] Assuming a tar yield of 70 lbs. per ton of coal and from this naphthalene yield of 3 per cent.

[9] Press Notice 13,819, U. S. Geological Survey, October 31, 1922.

[10] Communication from E. W. Dean.

[11] Müller, "Petroleum," **1910**, p. 356; Lunge, *Loc. cit.*, p. 678

These difficulties have, however, been successfully solved, and to-day the application of such oils in these engines abroad probably constitutes the most important fuel application of coal-tar distillates. In European practice such application compares very favorably with the use of petroleum oils in these engines, because of the lower cost.[12] This cost differential spurred the research which led to the early adaptation of the Diesel engine for this fuel.

Mechanism of Diesel Engine—To understand the problems involved, it may be well to refer briefly to the mechanism of the Diesel engine. Unlike the familiar explosion engine, the combustion is here prolonged at constant pressure, and the initiation of combustion is not dependent upon an external source of heat, but the fuel is automatically ignited by the high heat of the air in the cylinder. Diesel engines usually operate under an air compression of 450 to 500 lbs. per sq. in. and as a result the air becomes highly heated, its temperature rising to about 540° C. When the piston reaches its upper dead center, the fuel injection valve is opened and liquid fuel, in a volume proportional to the load of the engine, is forced by compressed air into the cylinder, where upon meeting the highly heated air contained therein it ignites and burns. Efficient and flexible operation require, of course, a proper blending of the fuel and air. This is secured primarily by atomization of the oil, and secondarily, by diffusion of the oil gas produced by thermal decomposition of the fuel prior to its combustion. The air-fuel limits within which combustion may occur, the temperature at which the combustion is initiated, and the rate of propagation of combustion are functions of the amount and chemical composition of the oil-gas produced, and these are determined in turn by the chemical composition of the fuel oil. Experience has shown that the paraffin oils with distillation ranges chiefly between 200° and 400° C. give oil gases which possess the more satisfactory combustion characteristics.[13] At 450° to 500° C. these lend themselves readily to the formation of an oil gas having a relatively high hydrogen content.

Coal-tar distillates consist chiefly of aromatic hydrocarbons of the ring type, of high stability and low hydrogen content (6.9 per cent as against 11.5 per cent) for petroleum oils.[14] They yield an oil gas only at comparatively high temperatures and then relatively slowly,[15] and of course give much less hydrogen than do the paraffin oils. Consequently, they have a high ignition temperature (480° C. as against 260° C. for the gas from petroleum oil). Thus, an engine which starts readily with paraffin oil, and which remains in operation under low load conditions, may not start at all with coal-tar oil, or if in operation, may stop when lower compressions lower the temperature of the cylinder. This difficulty is especially important with small engines, which radiate their heat rapidly.

To overcome combustion troubles, the usual practice is to utilize a petroleum oil for the primary ignition. One method is to start the engine on such an oil. After the engine has become hot, the supply of petroleum oil is discontinued and tar oil used. The governor and fuel pump are so designed that with a lowering of the load the fuel is changed to the petroleum oil, and vice versa. The second method involves the use of both oils simultaneously, the petroleum oil being stored around the edge of the end of the fuel valve, where it will always enter the combustion space first and so initiate the ignition of the fuel charge. The proportion of ignition oil to tar oil varies with the load, at no load being as high as 20 per cent, at half load 10 per cent, at three-quarters 4 per cent, and at full load 3 per cent. The average consumption is usually 7 per cent, and seldom exceeds 10 per cent.[16] The total fuel consumption on a heating-value

[12] According to Haas, *Bur. Mines, Bull.* **156**, 89, tar oil is the principal fuel for Diesel engines in Germany where about 1,000,000 h. p. is represented.

[13] Haas, *Loc. cit.*, especially p. 80.

[14] Moore, *Diesel Engine Users' Assoc., Report*, May 26, 1918; *C. A.*, **13** (1919), 1011.

[15] Neumann (*Z. Ver. deut. Ing.*, **62** (1918), 706, 722, 763; *C. A.*, **13** (1919), 2995) finds that the respective velocities of the formation of oil gas from paraffin oil, heavy coal-tar oil, and anthracene oil are as 10:2:1.

[16] Haas, *Bur. Mines, Bull.* **156**, 45.

basis is nearly the same as when petroleum oil alone is used.[17] According to Moore[14] the thermal efficiency may be greater than with petroleum oil. Diesel installations generally consume between 7000 and 8000 B. t. u. per brake-horsepower-hour, depending upon the size of the installation.

It is impossible to consider here many of the various expedients which have been suggested for assisting the combustion of tar oils in the Diesel engine. Many articles upon this subject have appeared, among which may be mentioned that of Moore.[14] The thermodynamic production of oil gas for Diesel engines has been considered by Neumann.[15]

Allner[18] reports the operation of Diesel engines on tar oil without the use of ignition oil. Lunge[19] states that oven tar oils of lower boiling point (150° to 180° C.) may be employed as ignition oils.

Crude Tars

Crude tars can generally be obtained at about half the price of their distillates. Accordingly, the use of tars as a fuel for Diesel engines has been given some study. Miaskowski[20] mentions a 100 brake-horsepower, horizontal Diesel engine which has been running for one year on ordinary coke-oven tar. Allner[18] states that one firm ran a 40-horsepower Diesel engine for 36 hrs. continuously, using both vertical-retort tar and certain kinds of retort-oven tar, wholly avoiding the use of any ignition oil.

However, the use of tars directly presents several disadvantages. Among these are high-ignition temperatures, varying per cents of free carbon, formation of gummy deposits on the fuel-pump valves and the fuel-valve stems, precipitation of carbon on the exhaust valves, wear of piston rings and liner due to the presence of ash, presence of water, and poor atomization due to high viscosity.[21] Horizontal- and inclined-retort and coke-oven tars are, therefore, generally considered unsatisfactory fuels, but tars from intermittent and continuous vertical retorts are relatively much less viscous, contain less free carbon, yield less coke, and are much richer in aliphatic compounds; such tars can be used directly without difficulty, especially if an auxiliary ignition oil is used.[22] The valuable properties of vertical-retort tar result from the low temperature under which these tars are distilled from the coal.

Low-temperature tar,[23] lignite and peat tars, and oil-gas tars are likewise suitable for use in the Diesel engine directly.

A description of an installation which supplied hot filtered tar to two 100-horsepower Diesel engines worked alternately is given by Schertel.[24] According to this author, the equipment ran with complete success for three years. Paraffin oil, when available, was used as an ignition oil, but occasionally the tar was used alone.

Coal-Tar Pitch

The abundant resources of petroleum in the United States have hitherto supplied this nation's need for fuel for internal-combustion engines, but these resources may be decreased. On the other hand, the carbonization of coal in recovery apparatus is increasing constantly so that this nation is passing into an era where the utilization of tar distillates as a source of fuel for internal-combustion engines may be both economic and important. Indeed, for certain tar producers, favorably situated with regard to their coal supply, that era may be said to be at hand. To such producers this utilization possesses an advantage which ranks with the economic advantage in that it aids in minimizing the possibility for external interruption of essential means of transportation.

Over 87 per cent of the coal tar produced in the United States in 1920 was derived from coke-oven tar, and of the remaining coal-gas tar there is a large percentage of horizontal- and inclined-retort tar. As indicated, the utilization of coal tar for Diesel fuel is, therefore, essentially a problem involving distillation. Since 50 to 70 per cent of the tar charged into the still must later be disposed of in the form of pitch, this utilization must carry "the burden of the pitch."

While the uses of coal-tar pitch are many, diverse, and constantly increasing, a large producer of coal tar must give preference to uses which will consume regularly a large quantity of pitch of uniform quality, with a minimum of handling and sales effort. Apparently, this means that his efforts must be directed towards the disposal of the pitch as fuel.

Pitch may be supplied to the combustion zone either as a solid or a fluid. To burn pitch in solid form it may either be coked and fired on ordinary grates, or it may be subdivided and blown in with the air blast, somewhat as in the burning of powdered coal. The pulverizing of pitch may present some difficulty, and to eliminate this difficulty, one process consists in melting the pitch, dividing it into drops, and allowing them to fall into a cooling medium.[25]

Very recently a process has been developed by E. W. Clarke,[26] whereby pitch having a melting point of 82° C. or higher is powdered with impact pulverizers, just before the furnace (the velocity and direction of the air blast preventing any appreciable sticking). The furnace settings are the same as those for powdered coal, but special burners have been devised and are in successful operation.

Pitches of very high melting points (preferably 130° C. or higher) may be coked, yielding a solid fuel which possesses all the advantages of coke from coal, and in addition certain advantages derived from its low ash content. In the Birmingham district a quantity of such pitch coke is prepared in beehive ovens. Contamination from the refractories of the oven is avoided in a process which has been developed in the course of coöperative researches conducted by the Koppers Co., the Aluminum Company of America, and the American Tar Products Company. This process and the apparatus employing it have been in successful operation by the American Tar Products Company and are the subject of issued and pending patents owned by that company.

If desired, the producer of the tar may mix the pitch with the coal going to his retorts. Here the only restriction imposed upon the pitch is that it be sufficiently brittle to permit it to be broken up conveniently. If all of the pitch is returned to the oven, its average weight is approximately 2 per cent of the coal charged. Pitch so added is converted into useful products, gas, tar, and coke, and the desirable qualities of the coke produced from the coal alone do not seem to be adversely affected. Indeed, the quality of the coke may be improved. Thus, Becker[27] has shown that good coke may be made from certain noncoking coals by the admixture of from 2 to 10 per cent of pitch.

The burning of a mixture consisting of 18 per cent pitch, 75 per cent breeze, and 7 per cent coal on an ordinary grate

[17] Tar oils have a thermal value of approximately 16,000 to 17,000 B. t. u. per lb., while petroleum oils have a value of at least 18,000 B. t. u. per lb.

[18] *J. Gasbel.*, **54** (1911), 1025, 1051; *C. A.*, **6** (1912), 1065.

[19] Lunge, "Coal Tar and Ammonia," **1916**, p. 678.

[20] *Engineering*, **93** (1912), 384; *C. A.*, **6** (1912), 1984.

[21] Moore, *Engineering*, **108** (1919), 167; *C. A.*, **13** (1919), 2755.

[22] Allner, *Loc. cit.*, also *J. Gasbel.*, **54** (1911), 321; *C. A.*, **5** (1911), 2321; also *J. Gas Lighting*, **115** (1911), 106; *C. A.*, **5** (1911), 3333. Moore, *Petroleum World*, **14** (1917), 213; *C. A.*, **11** (1917), 2730; also *Engineering*, **108** (1919), 167; *C. A.*, **13** (1919), 2755. Schlaepfer, U. S. Patent 1,183,038, May 16, 1916; *C. A.*, **10** (1916), 1787.

[23] *Gas World*, **75** (1921), 3; *C. A.*, **15** (1921), 2707.

[24] *J. Gasbel*, **61** (1918), 493; *C. A.*, **13** (1919), 1012.

[25] Barrett Mfg. Co., Ger. Patent 286,549, November 8, 1913; *C. A.*, **10** (1916), 1787.

[26] Communication to the writer.

[27] U. S. Patent 1,182,738, May 9, 1916

is described by Kershaw.[28] The pitch is fed upon a special type of fire bar consisting of a channeled trough sloping slightly from the front to the back of the grate. The same writer mentions the use of pitch in internal-combustion engines in mixture with creosote oil, and claims that satisfactory operation is obtained by the aid of pilot ignition, using 5 per cent of petroleum oil.

The use of pitch as a liquid fuel is closely related to the use of tar directly. In 1920 more than 46 per cent of all the coal-gas and coke-oven tar produced in the United States was consumed at the point of origin,[1] largely or entirely as fuel. This large consumption is due chiefly to the popularity of coke-oven tar as a source of fuel for the open-hearth furnace. Here the liquid tar is supplied to a burner or gun where it is atomized under 50 lbs. steam pressure. The flame is thin and light and much hotter than that from producer gas, the tonnage of the furnace is increased, and the fuel consumption diminished. (In mixed metal practice which has come under the writer's observation, 5 B. t. u. in the form of tar were equivalent to approximately 8 B. t. u. in the form of coal charged to producers, and between 6 and 6.5 B. t. u. in the form of producer gas.) The construction of the furnace is much simplified. Moreover, tar possesses the advantage that it can be used in furnaces in which the gas sewers are burned out, and that it can be stored for use in those plants which are confronted by a seasonal natural-gas shortage.[29]

Owners of open-hearth furnaces would welcome the pitch in a form as satisfactory as that of the tar. This involves the burning of a soft pitch. Essential factors are the viscosities of the tar and pitch and the yield of tar oil. The change in density is not serious. Under certain conditions tars and pitches undergo very great reduction in their viscosity when heated, and this property is utilized daily in the handling of these materials, but the literature contains very little information upon the rate of change of viscosity with temperature and the magnitude of the change in viscosity with changes in the amount of oil removed.

This problem is considered in another paper,[30] by the writer, which gives technical values for the viscosities of a number of coke-oven tars and their soft pitches at a number of temperatures near the sharp bend in the viscosity-temperature curve, together with mathematical interpolation formulas which permit the calculation of approximate viscosities at various other temperatures and oil yields.

The economic recovery of Diesel fuel distillates with the production of a uniform grade of pitch can best be obtained by a process of continuous distillation. A continuous still has recently been developed which is very suitable for this purpose. The design appears to present a large number of very desirable features, among which may be mentioned the following:

1—Heat is applied upon vertical surfaces only, thereby eliminating high temperatures at points which may be coated with insulating solids deposited by the heated tar. By eliminating "burned out" still bottoms, the life of the still should be materially increased.

2—The entire still charge is subjected to a violent thermal agitation which effectively scours loose débris from all surfaces and prevents its redeposition. This agitation also diminishes local overheating with attendant coke formation, and tends to increase the oil yield and diminish the pitch yield.

3—The ratio of heat-transfer surface to the volume of still is very large, permitting high rates of distillation with small installations and without exposing large volumes of tar to the heat.

4—The absence of local overheating should materially aid in fractionation. The design includes other features which should assist in this, a desideratum not approximated by many designs of continuous tar stills.

Extent of Coal-Tar Resources

If all the coke-oven and coal-gas tar burned or otherwise consumed by the producers in the United States in 1920—calculated as the difference between the tar produced and the tar sold—had been treated in a continuous still for the removal of oil equivalent to 25 per cent of its volume and the production of soft pitch, there would have been obtained about 48,000,000 gal. of distillate, or sufficient fuel to furnish over 100,000 horsepower-years, if the entire distillate were fed to Diesel engines. This, of course, is only a very small fraction of the power which might have been produced from other oil resources. However, by-products from such a distillation might assist materially in overcoming shortages in other fields. Thus, there is to-day a serious shortage of cresol and phenol. If the tar mentioned above contained approximately 2 per cent of phenol plus cresol, there would be available a total of approximately 30,000,000 lbs. of these—sufficient to completely overcome this shortage. Crediting these to the process and assuming reasonable costs and the maintenance of reasonable price levels, it can be shown that the producer would secure his Diesel fuel at little or no expense, as a profit for the operation.

Suggestion for Further Research

In closing this account of recent accomplishments bearing upon the use of coal tar as a fuel for internal-combustion engines, it is fitting to suggest for research one phase which apparently remains rich in unsolved problems and poor in accomplishments—namely, the utilization of coal-tar pitches directly for the manufacturer of producer gas. Von der Forst[31] states that the tar oils have been used for this purpose in the United States. If so, this is the only instance of such use which has come to the writer's attention and this use is certainly not extensive. Various processes for gasifying pitch directly have been proposed, but so far as the writer is aware, none have been sufficiently successful to warrant wide-spread adoption.

[28] *Gas World*, **68** (1918), 234; *C. A.*, **12** (1918), 1416.

[29] Ferguson, *Chem. Met. Eng.*, **21** (1919), 610; *C. A.*, **14** (1920), 520.

[30] "The Viscosity of Coke-Oven Tars and Soft Pitches." Presented before the Section of Gas and Fuel Chemistry at the New Haven meeting.

[31] *Stahl u. Eisen*, **31** (1911), 1552; *C. A.*, **6** (1912), 1670.

The Magic Wand[1]

By Harvey A. Neville

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The inevitable lecture experiment and popular trick of "changing water into wine" may be convincingly accomplished by means of a stirring rod made of glass tubing. This instrument, as shown in the accompanying drawing, is easily constructed as follows:

The ends of a piece of glass tubing of any convenient size and length are almost closed by heating them carefully in a small flame. The middle portion of the tube is then heated until it collapses and the tubing is pushed toward the center to thicken and close it. One end is to be filled with an acid and the other with an alkali solution. This is done by heating the chamber to drive out some of the air and placing the end in the solution. The liquid which enters is boiled to drive out the remaining air and the solution will now fill the reservoir completely. With phenolphthalein as indicator the color may be made and destroyed by alternating the ends of the stirring rod, the change being made surreptitiously while wiping with a towel. The openings should be so small that the liquids will not drop out, but the acid or alkali will diffuse through.

The mystery may be increased by having the acid red (methyl orange) and the alkali blue (ammoniacal copper salt). Other combinations will occur to anyone.

[1] Received April 2, 1923.

Examination of Writing Inks[1]

By F. F. Rupert[2]

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There is need of a system for examining writing inks based on scientific principles and also related to the needs of the average user of ink. This paper attempts to provide such a basis. The four qualities of writing inks most desired are color, permanence, stability, and noncorrosiveness. The relation of the composition of ink to each of these properties has been studied. The tests now in use, with modifications, are recommended, with emphasis on the more practical tests. A system of rating which gives equal weight to the four fundamental properties is suggested. Only iron tannate ink is considered in full, but the properties of other inks are discussed briefly.

The only system of testing inks yet published is especially designed for use in government and other records in which permanence is paramount. This system was devised by Schluttig and Neumann,[3] many of whose recommendations were adopted by the Prussian government in 1888. Substantially the same methods, with additions, have been adopted in the United States for testing inks for government use. By these methods, which are described in government publications,[4] the inks to be examined are compared with a standard ink having the following composition:

	Grams
Tannic acid	23.4
Gallic acid	7.7
Ferrous sulfate	30.0
Dilute hydrochloric acid, U. S. P. (10%)	25.0
Phenol	1.0
Suitable blue dye	2.2
Water to make a volume of 1000 cc. at 15.6° C.	

This formula differs from that originally given by Schluttig and Neumann only in the omission of gum arabic. It differs from that of most commercial writing inks in that it contains two or three times more of all the ingredients except hydrochloric acid and dye. Each property of this ink is taken as a standard to be equaled or exceeded by the ink under examination.

In a system of rating suggested in the earlier government reports, figures were to be applied to each ink and the sum of the figures thus obtained was to be considered as the final rating of the ink. The standard ink was to be rated as follows: exposure to sunlight, 70; exposure to reagents, 10; keeping quality, penetration, stickiness, fluidity, and action on steel pens, 15; composition, 5. No quantitative methods of rating are recommended in the most recent publication.

The principal objection to the government procedure, as applied to ink for ordinary use, is that the keeping quality of standard ink, or "iron-gall" ink having the same degree of permanence, is poor. It deposits sediment rather quickly, and is also corrosive. Ink of similar composition offered to the public has proved decidedly unpopular.

Properties of Ink

The required properties of a serviceable ink may be grouped under four heads—color, permanence, stability, and noncorrosiveness. "Permanence" refers to the ink after it has been applied to paper; "stability" refers to the keeping quality of the liquid. These qualities are emphasized differently, according to the use to be made of the ink. In government and other legal record work, permanence is the chief requirement; for social correspondence, color is perhaps most important; when steel pens are used, as in accounting, noncorrosiveness is a great factor; and for fountain pens stability is highly desirable.

Most of the ink used for writing is iron tannate ink, prepared from a ferrous salt and either tannic and gallic acids or nutgall extract. Therefore, only iron tannate ink is considered here, unless otherwise stated. Other classes of ink to be mentioned briefly are as follows:

Acid logwood inks, containing chiefly logwood extract and a chromium, iron, or aluminium salt, usually potassium chromate, in acid solution.

Acid logwood inks with suspended matter, which contain black suspended matter, in addition to the ingredients found in the first class.

Alkaline logwood inks, which contain logwood extract and potassium chromate in alkaline solution.

Carbon inks, which consist of very fine suspensions of carbon, with the necessary suspending agents.

Prussian blue inks, which are simply solutions of soluble Prussian blue.

Aniline-dye inks, which contain only soluble dyes.

Color

Marks made by any ink should be easily legible and the color should be pleasing. The color of "colored" inks, which are merely solutions of aniline dyes, depends entirely on the dye. Chrome-logwood inks usually are dark violet or violet-black, while carbon inks are brownish black. Iron tannate inks are peculiar in that several days are required for the complete development of the insoluble ferric tannate which acts as the permanent dye, the writing being almost colorless at first.

The addition of a dye to impart a preliminary color, then, is imperative. This dye is usually blue; hence, the ordinary "blue-black" inks. "Red-black" iron tannate inks are also made, and "black-black" inks, which contain an added black dye, are gaining in popularity. Indigo carmine was used as the preliminary blue dye in the early blue-black inks, but it has been largely replaced by "soluble blue," a sulfonated triphenylrosaniline.

When iron tannate ink dries on paper, it is exposed to a relatively large amount of air. Consequently, the ferrous salt begins to oxidize to the ferric salt, which reacts with the tannic and gallic acids to form an insoluble compound of high coloring power and affinity for the fiber. This process is accelerated by partial loss of the hydrochloric acid, although some of the acidity may be retained for a long time. The maximum oxidation requires several days in diffused daylight, and longer in the dark. The process is accelerated by direct sunlight, and also by alkalies, through the neutralization of the excess acid, although an excess of alkali may produce undesirable effects, such as fading of the dye. The final color is affected

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

[2] Industrial Fellow, Mellon Institute of Industrial Research.

[3] "Die Eisengallustinten," Dresden, 1890.

[4] Walker, "Some Technical Methods of Testing Miscellaneous Supplies," U. S. Dept. Agr., *Bur. Chem., Bull.* **109** (1908); U. S. Dept. Commerce, *Bur. Standards, Miscell. Pub.* **15**. "Inks—Their Composition, Manufacture, and Methods of Testing," U. S. Dept. Commerce, *Bur. Standards, Circ.* **95** (1920).

by the quantities and proportions of ferrous salt, tannic acid, gallic acid, hydrochloric acid, and dye. Beginning with a composition approximating that ordinarily used, the color is darkened by the addition of gallic acid, tannic acid, or ferrous sulfate—most easily by gallic acid. It is also darkened by replacing the tannic acid by gallic acid, even if the substitution is made in the proportions of their molecular weights. Increasing the hydrochloric acid makes the color paler by retarding indefinitely the oxidation of the ferrous ion.

Beyond the requirements of legibility, the choice between inks with respect to temporary color is largely a matter of personal preference. A deep permanent color is essential, as it indicates a high iron tannate content and therefore a high degree of permanence.

Permanence

The first practical requirement for permanence is that the record must not be effaced in the dark, or upon moderate exposure to light, for many years. If it will endure for centuries, so much the better. Permanence under exposure to direct sunlight is less essential. If the effect of sunlight is to accelerate reactions that occur slowly in the dark and tend to destroy the ink, exposure to sunlight constitutes the best test for the ink. That point, however, is by no means settled. The permanence of an ink should not be destroyed by water, so that even several thorough drenchings, such as may occur in case of fire or by the falling of papers into water, will not seriously impair the legibility of the record.

Resistance to erasure by reagents is highly desirable, but iron tannate ink of any practicable strength may be removed by alternate applications of acid and hypochlorite solution.

The most severe test of the permanence of ink consists in exposure to weather, involving successive exposure to light and water. For practical purposes, it is not necessary that an ink survive such treatment for months or weeks, but it should give an excellent indication of permanence. Such a test shows that aniline-dye inks are very easily removed and that chrome-logwood products have the same general degree of permanency as iron tannate inks, while carbon and Prussian blue inks remain almost unchanged when an iron tannate ink, even of the Schluttig and Neumann standard strength, is effaced completely. Carbon inks must be thoroughly dried on the paper, as they are easily removed by blotting.

When streaks of iron tannate inks of varying composition were exposed, on a nearly horizontal surface, to the elements for several months, or until the streaks were entirely effaced, in summer, an ink of the "standard" composition was to a large extent removed in 6 wks. and entirely removed in 10 wks. Nearly all of an ink of half the "standard" strength was removed in 6 wks. In winter the effacement of the stripes is naturally much slower. The permanence of iron tannate ink is independent of the acidity. The streaks made of inks differing only in acidity, although varying in color, had the same final appearance and persisted for the same time, evidently on account of the removal of nonvolatile, but soluble, acids. Similar relations hold true when the amount of tannic acid is increased. In an extreme case, an ink with a low ferrous sulfate and high tannic acid content (8 and 28 g. per liter, respectively) had a pale color before the test, but, after prolonged exposure to weather, it was much darker than it was originally. The permanence of inks containing gallic acid without tannic acid is very low; that of ink containing both of these acids increases with the amount of tannic acid. Where the gallic acid content approaches zero, there is a drop in the permanence curve.

The test of permanence often given greatest consideration consists in exposure to strong light. Experimental evidence, however, shows that when the ink is exposed to sunlight over short periods, such as 1 mo., the principal result is the fading of the dye, leaving a gray color. After a longer exposure, such as 3 mo., a change toward brown takes place, becoming more noticeable as the strength of the ink is decreased. As Schluttig and Neumann have pointed out, this is due to the decomposition of the ferric tannate, with formation of ferric oxide. In the fading of the dye, which occurs in a comparatively brief period, there is a marked difference between the resistance of different dyes. Where artificial light is used, the relative effects are practically the same.

When a streak of undyed iron tannate ink is exposed to water for short periods, such as 1 to 24 hrs., the only change noticeable is one in color from very dull violet-blue to dull violet. When dye is present, it is removed to an extent dependent on its nature. Some dyes blur or penetrate the paper near the ink mark, while others retain the original clear outlines. Upon longer exposure, the change is progressive, but slow. Logwood, carbon, and Prussian blue inks undergo little change on exposure to water, but aniline-dye inks, with the exception of those made from nigrosine, are easily removed. Logwood ink possesses its full degree of resistance to water as soon as it dries.

On iron tannate and logwood inks the hypochlorite test gives results closely paralleling those obtained by exposure to weather. The test with acid is of little importance, as the iron tannate dissolves, leaving the dye, which is usually partly insoluble in the acid, and the test only indicates the nature and concentration of the dye. The test with ammonia or any other alkali gives very little information not afforded by the test with water. The iron tannate is partly destroyed, changing to a brownish color, and the dye is removed or changes color according to its nature. Carbon inks are very resistant to all the reagents. Prussian blue inks are highly resistant to acids, but are removed by alkalies and by hypochlorites.

Stability

Ink in a closed bottle should remain fluid and free from sediment indefinitely. Ink left in a partly opened bottle or in an inkwell is subjected to three influences—oxidation of the ferrous ion to the ferric ion, which then forms an insoluble compound with the tannin; oxidation of the tannin, with subsequent formation of insoluble condensation products; and evaporation of the ink. In an inkwell, evaporation usually is the most rapid process, unless the ink is very unstable. Although there is no particular trouble from sedimentation, a point is reached where so much water has been evaporated that the solution becomes saturated with respect to some of the ingredients which begin to separate. Much of the difficulty from ink in wells arises from neglect to clean the walls regularly. For fountain pens, freedom from sediment is absolutely essential.

The stability of ink is affected by all the factors of its composition. The principal type of instability in iron tannate ink is the formation of insoluble ferric tannate or of condensation products of tannic acid, which appear as a sediment on the sides and bottom of the bottle. The stability of such ink depends largely on the ratio of hydrochloric acid to ferrous sulfate, increasing with the increase in acid. The stability may be measured by closed tests and by open tests which will be described later. The two tests may give different results, indicating that the sedimentation is not always due to the same cause. Where the concentration of all ingredients is high, as in the "standard" ink, a slight sediment is usually found in the closed test. At very low total concentrations, such as 8 g. of ferrous sulfate per liter, little sediment forms. Between these two extremes, a nearly constant ratio of hydrochloric acid to ferrous sulfate is necessary to prevent sedimen-

tation, whatever the concentration. The Schluttig and Neumann standard ink would be improved in this respect by the addition of more hydrochloric acid, although at the expense of noncorrosiveness. The stability is also increased slightly by the further addition of tannic acid. Soluble blue, the dye usually employed, and a number of direct blues increase the stability of the ink, but indigo carmine does not. This effect is not due to the exclusion of light.

Gum arabic was formerly included in all formulas for iron-gall ink, with the primary object of retarding sedimentation. Recently, however, it has been found unnecessary by several experimenters, and it is no longer included in the government standard formula or in the working formulas of some of the manufacturers.

Mold—another source of instability—is effectively prevented by the phenol commonly employed.

Acid logwood inks readily acquire sediment on standing. Alkaline logwood inks do not, but they lose color by oxidation. Carbon inks tend to settle on standing. Prussian blue inks and aniline-dye inks remain clear.

Noncorrosiveness

A noncorrosive iron tannate ink, as far as is known at present, cannot be prepared, since acidity is necessary to prevent rapid oxidation of the ink in the bottle. The practical requirement for corrosion must be the lowest degree consistent with satisfactory permanence, stability, and color.

Corrosiveness depends primarily on the amount of hydrochloric acid in the ink. The exact relationship depends upon the method of estimating corrosion. If the pen is immersed in a large quantity of ink, the loss in weight is approximately proportional to the hydrogen-ion concentration. If, as in the customary test, a pen weighing 0.3 to 0.6 g. is put in 15 to 30 cc. of the ink, the acid becomes exhausted within three or four days, and the total loss is proportional to the total amount of hydrochloric acid present.

In a number of experiments plain steel pens were immersed in solutions of hydrochloric and other acids of definite concentrations, and in inks containing varying amounts of such acids, for different lengths of time. In the acid solution, an amount of iron equivalent to the total acidity of the solution was dissolved within 3 days at most. Then followed a slow, steady, and very slight loss, due to "rusting" (oxidation by dissolved oxygen or water itself). In inks, the time required to reach the maximum was slightly greater. This was followed by a gradual loss which was independent of the original acid concentration, but of greater extent than the rusting noted in the experiments with acids. The loss was caused by the action of the tannic and gallic acids. This observation was confirmed in another experiment in which tannic and gallic acids alone were used in the solution. When the ink contains the usual dye (soluble blue), the loss at any particular time is smaller, indicating that dye has a protective action. It has been shown that this is a chemical effect of the dye, and is not due to protection from light.

In addition to tests conducted by immersing the pen in the ink for definite periods, some experiments have also been made by a mechanical tester, in which the pen is dipped in the ink at definite intervals, between which the ink is allowed to dry on the pen. So far as these tests have gone, the same general relations have been found true.

Most coated, bronzed, and plated pens are very little more resistant to the action of acid than uncoated steel pens. At the point and slit of the pen, where plating is difficult, the acid quickly reaches exposed spots and the plating is gradually undermined. A marked difference has been found in the resistance of plated pens from different manufacturers. The final solution of the corrosion problem lies in the hands of pen manufacturers. Some new alloy steels offer possibilities for beneficial results.

The other classes of inks mentioned are practically noncorrosive, except acid logwood inks, which are generally corrosive, although less so than iron tannate inks.

"Building on the pen," or precipitation, is often erroneously called corrosion. In fact, complaints about "excessive corrosion" have arisen concerning inks deficient in acidity, with consequent ready precipitation of ferric tannate and dye upon the pen.

Relation of Properties to Composition

The properties of the various classes of inks already described may be summarized as follows:

	Color	Permanence	Stability	Corrosiveness
Acid logwood.....	Violet	Good	Poor	Slight
Alkaline logwood...	Blue-black	Good	Poor	None
Carbon.....	Brown-black	Very good	Fair	None
Logwood with suspended matter...	Brown-black	Good	Poor	Slight
Prussian blue.....	Greenish blue	Good	Good	None
Nigrosine.....	Violet-black	Fair	Good	None
Other aniline dyes..	Various	Poor	Good	None

The following relations for the properties of iron tannate inks hold true: The immediate color depends only upon the dye; the permanent color depends only upon the concentrations of ferrous sulfate, tannic acid, gallic acid especially, and the dye, but is decreased by an excess of hydrochloric acid; permanence, as judged by the weather test, depends on the ferrous sulfate, gallic acid, and especially tannic acid, and is independent of the amount of hydrochloric acid; stability, which is in general augmented by increase of acid, depends on the ratio of hydrochloric acid to iron, and is slightly increased by increasing the tannic acid and by the presence of certain dyes; corrosion depends primarily upon the hydrochloric acid, but the tannic and gallic acids are also factors and the dye acts as a protective medium. Conversely, these relations are: The function of ferrous sulfate and of tannic and gallic acids is to furnish the foundation for the ink, thus affecting directly the permanent color and permanence, but stability is decreased as concentration is increased. Tannic acid increases permanence, while gallic acid heightens developed color. Both increase corrosion slightly. Hydrochloric acid increases corrosion and stability and lightens the color, but does not affect permanence. The dye imparts a preliminary color and retards sedimentation and corrosion. Phenol acts only as a preservative.

Testing Ink

A complete examination of ink calls for two methods, the analytical and the practical. The analytical method includes the determination of all the essential constituents—iron, tannic and gallic acids, total solids, ash, and acidity. The specific gravity is also useful as an indication of the total amount of dissolved material present. The practical method should include determinations of the four essential characteristics—color, permanence, stability, and corrosiveness.

Although both methods are necessary for a complete scientific examination, the practical method should suffice for a test and comparison of inks for use for any definite purpose. The behavior of the ink may be predicted from a complete analysis, provided the relations of properties to composition have been thoroughly established, but the relationships are often complex.

Full and satisfactory directions for analytical tests are given in publications of the Bureau of Standards.[5] In the determination of iron, the volumetric method, as recommended in the earlier literature, may be preferable. More

[5] *Loc. cit.*

complete directions for the volumetric method may be adapted from the procedure described by Low.[6]

Practical Methods

The practical methods are given in the order in which they may be begun most efficiently. Before conducting any of the tests, the sample should be filtered. Unfiltered inks may give undeservedly high results in permanence on account of insoluble material, which is sometimes very slow in settling. Any excessive sedimentation should be observed in connection with the stability test.

Streak Tests—According to the practice of the Bureau of Standards, a sheet of bond paper of good quality, 27 cm. (11 in.) long, is stretched over a flat piece of glass with parallel edges about 20 cm. (8 in.) apart, holding the paper in place by clamps attached to the projecting ends of the paper and to each other by means of a rubber band. (The author has used a flat board, to which the paper is affixed by means of thumb tacks, but the paper is likely to wrinkle, making the streaks uneven.) The glass is then placed in a secure position at an angle of 45 degrees to the horizontal, so that the ink will flow lengthwise of the paper. A pipet is made from a glass tube about 25 cm. long and close to 3.5 mm. in diameter, by making a file mark 62 mm. from the lower end. This holds about 0.6 cc. of ink from the file mark down. The ink to be tested is drawn up in the pipet to the mark. Then the pipet is held vertically near the top of the paper, with the lower end almost touching the paper, and the ink is released. It is well to make several streaks of each ink.

Penetration and Fluidity—The ink should penetrate into the fibers of the paper, but should not pass through it. A good idea of fluidity can be formed by observing the head of the streaks if they are carefully made. A normal ink should give an oval head, and the rest should be nearly uniform in width; a very fluid ink gives a wide head and the streak rapidly narrows. Usually there is not much difference in the fluidity of ordinary inks. A wavy streak indicates only that the paper is slightly warped, and usually does not appear if the directions are followed. Any stickiness should also be observed.

Temporary Color—The inks are compared soon after making the streaks and are ranked in the order of the best colors. The mark made by the ink should, of course, be dark enough to be plainly noticeable. Beyond that point the comparison is wholly a matter of judgment and personal preference. A streaked or speckled appearance indicates that the ink contains dye which is not in solution.

Permanent Color—The streaks are exposed to diffused light for 7 days, in an atmosphere free from chemical fumes and excessive dust. If desired, samples of writing may be made with the ink at the same time and exposed similarly. However, streaks show slight differences between inks more easily. The color is again observed. Comparison may be made by means of the use of a standard ink, such as that recommended by Schluttig and Neumann, colored with a suitable blue dye, but it is often difficult on account of differences between the dyes. In preparation for the exposure tests, the paper is cut into crosswise strips of uniform width, preferably 1 in. The top and bottom strips, at least, are preserved as blanks.

Exposure to Light—One strip is exposed in a position where it will receive as much sunlight as possible, for at least 2 wks., or as long as necessary to establish differences between the permanence of the inks. If ultra-violet light is obtainable, the streaks may be exposed at a short distance from the source of light, for 48 hrs. or longer. A nitrogen-filled, 100-watt tungsten lamp may be used as the source of light in the same way. An exposure to ultra-violet light part of the time and to the tungsten lamp part of the time gives the nearest approximation to sunlight. In the exposure to artificial light, care must be taken to arrange the paper so that the different streaks will receive equal illumination. A light test for permanence is not very effective unless conducted for several months.

Exposure to Weather—If this test is to be applied, one of the strips is exposed where it will be subjected to the action of the weather, in a place as free as possible from dust and smoke. The progress of the test is noted at weekly intervals.

Exposure to Water and Reagents—Narrow strips are immersed in water, ammonia diluted 1 to 10, 2 per cent hydrochloric acid, and bleaching powder solution (or sodium hypochlorite solution) containing 0.005 N available chlorine. If sodium hypochlorite solution is used, the excess alkalinity should be nearly neutralized. Since the hypochlorite test is the most important, special care must be taken in its application. In this test the strips must be cut to the same uniform width, and the solution must be stirred frequently. The strips are observed from time to time. For inks which are easily removed, a good measure of permanence is the time required to remove all the ink except a pale yellow stain. For others the amount left after a given time is the best indication. The resistance of the dye should also be observed by the rate of disappearance of the blue color. It may be advantageous in some cases to vary the strength of the hypochlorite solution.

Stability—The ink should first be examined in the original bottle for evidences of sediment already developed. Then it is filtered and a small sample (say 15 cc.) is put in each of two small bottles. One is corked tight, while the other is covered with a filter paper. The bottles used in a test must be of the same shape and size. The condition of each is noted from day to day. Seven days suffice for the open-bottle test. At the end of the period each sample is again filtered and the relative amount of sediment is noted. Any sediment showing more than fine, loosely scattered flakes on the paper is to be regarded as excessive.

Corrosion (*Complete Immersion Method*)—The pens should be of unplated steel and must be of the same make and size. They should also be from the same box if possible. A small pen, such as "Spencerian No. 1," is entirely satisfactory, but large pens may give comparable results in a shorter time. If the samples are large enough, five tests of each ink should be made, in order to give the greatest accuracy, as there are often individual differences between the pens. However, two tests will ordinarily suffice. Twenty cc. or more of ink should be used for each test, unless only a small amount is available, in which case it is better to make two tests, for instance, with 10 cc. each, rather than one with 20 cc. Of course, the same quantity of ink must be used in each test in any comparison. The required amount of ink is put into each bottle, of appropriate size, and a pen, first cleaned with U. S. P. ethyl alcohol and ethyl ether and weighed to the nearest milligram, is put in each bottle. The bottles are loosely covered and allowed to stand for 7 days. Then the pens are removed, washed, rubbed with a cloth to remove all adhering matter, and weighed again, and the loss is recorded. A shorter time is not advisable, except possibly when large pens are used. In 7 days the mineral acid in the ink is exhausted and the action of the tannic and gallic acids has proceeded to a slight extent only. Experiments have been made in which the pens were first given a preliminary exposure to ink for one or two days, then weighed and exposed to a fresh portion of ink for one day. The results so far obtained are too irregular to justify the use of the method.

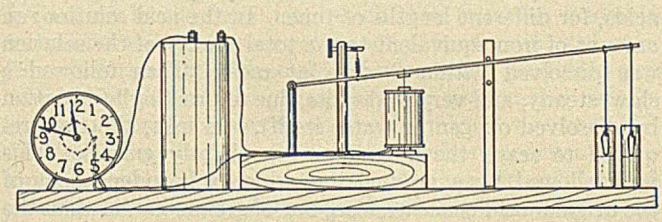


Fig. 1—Mechanical Ink Tester

Corrosion (*Mechanical Tester*)—Inks may be tested under more nearly working conditions with a device which dips the pens in the ink at intervals, allowing it to dry between the immersions. Such a device (Fig. 1) may consist of a clock, with a circular plate having four equidistant projections attached to the minute-hand shaft, a spring which makes contact with each projection for a few seconds as it is carried around, a dry cell and a 2-spool electromagnet of suitable strength and resistance, an aluminium bar 10 in. long, pivoted at one end so as to move vertically, an armature at the middle of the bar just over the electromagnet, a cross-bar at the other end to support the pens, and a brass spring (or a rubber band) to raise the bar when released. In the apparatus used by the author, four pens are supported from the bar and from the cross-bar, with iron wires passing through holes in the bars and through the eyes of the pens. Although the pens are in an inverted position, they are practically completely immersed when contact is made and just out of the ink when the bar is released. The ink is contained in four small jars, about 20 cc. being used in each vessel. A 5- to 7-day period affords sufficient time for the test. If there is plenty of ink for the test, greater losses are obtained by renewing the ink daily, but it is not necessary, and it is a question what method most nearly approaches actual conditions of use. Of course, in comparing inks by this

[6] "Technical Methods of Ore Analysis," 1914, p. 132.

method, they must be treated alike in this respect. The pens are prepared and weighed before being used and are cleaned and weighed after using, as in the other method.

The results obtained by the mechanical tester are usually in the same order as those from the closed test, but not in the same ratio. This has been found true especially in dealing with inks in which "negative catalyzers" were added to reduce corrosiveness. One of these substances reduced the corrosion to a very low value when the pen was immersed all the time, but the mechanical tester showed little improvement.

An estimation of the amount of "building on the pen," sometimes confused with corrosion, can be made by observing the appearance of the pen after it has been used in the mechanical tester for a day or longer.

Comparison and Rating

Up to this point nothing has been said about a standard for comparison or a system of rating. Strictly speaking, neither is absolutely necessary. If one ink is to be tested for possible use, a minimum standard can easily be set for it in each particular. If two or more are to be compared, they can be compared separately in all their qualities and an average made, with due consideration to the particular application of the ink. In some cases, where a number of inks are to be compared, however, the analyst may wish to have a numerical standard for reference.

The system of rating proposed in the earlier government publications is no longer recommended. Indeed, this procedure has been taken more seriously than was intended. It must be emphasized that there can be no hard and fast system of rating which applies to all cases.

The author's suggestion is that corrosiveness, stability, permanence, and color be graded 25 each, on a scale of 100. The standards for the separate headings are determined as follows:

Color—The initial color and final color are each rated on a scale of 12.5. An entirely satisfactory depth of color, obtained by an ink of known composition, is selected as a standard and graded 12.5. The same ink, diluted to a point where it is entirely unsatisfactory, is rated zero. The intermediate steps are obtained by mixing the two inks in the proper proportions, and the ink under examination is compared with the nearest standard. In the rating of color, especially the initial color, the question of personal preference naturally is a factor. It is suggested that several persons assist in this test, and, if possible, that the user of the ink pass upon the preference as to color.

Permanence—The results of the weather test or those of the hypochlorite test may be used. In either case the inks under examination are compared with a series of inks of known composition, varied by definite ratios of concentration. The ink is then compared with the nearest standard and so rated. The rating may be corrected for the effect of the persistence of the dye, if necessary.

Corrosion—High and low limits for loss in weight are chosen arbitrarily, with respect to the reasonable expectations for the ink. A rating of zero corresponds to the higher loss and a rating of 25 to the lower. The rating of the ink is determined by locating the position of the actual loss on this basis.

Stability—The sediment after a known period of exposure is collected on a filter paper. No sediment is rated 25 and a set maximum is rated 0. The amount estimated by comparison gives the basis for the rating of the ink. For an accurate test, the sediment may be collected in an alundum crucible and weighed.

The system of rating must in every case be subordinated to the knowledge of the purpose for which the ink is to be used. In the author's opinion, however, this system of rating establishes a criterion for the average user.

Apparatus for Dispensing Concentrated Sulfuric Acid and Sodium Hydroxide Solutions[1]

By Roscoe C. Abbott

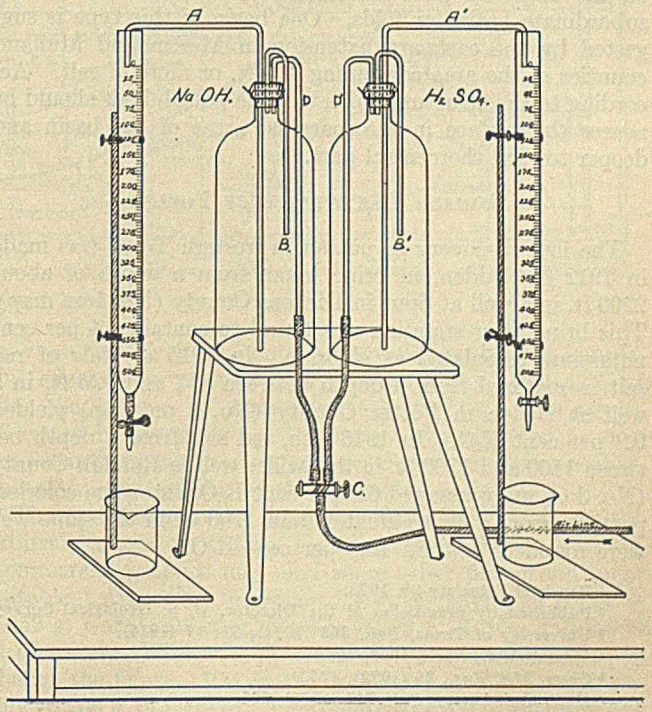
Experiment Station, Agricultural College, Lincoln, Neb.

The accompanying diagram shows a type of apparatus for dispensing concentrated sulfuric acid and sodium hydroxide solutions for the Kjeldahl nitrogen determination. This apparatus has been used in the feed laboratory at this station with complete success.

Two 500-cc. burets, graduated to 5 cc. with the 25-cc. divisions made prominent, are placed at such a height as to allow the mouth of an 800-cc. Kjeldahl flask to be easily placed beneath them. The beakers beneath are for the purpose of catching any drops of liquid that may drop, and are removed only at such times as may be necessary for cleaning up. Eight-liter bottles for the acid and alkali are fitted with 3-hole stoppers and placed on a shelf or box at such a height that the tubes AA′ extending from the bottom of the bottles may be bent at convenient angles and reach just to the zero mark of the burets. The tubes DD′ extend through the stopper and are connected to an air line by means of a 3-way stopcock, C. The source of air pressure may be either the laboratory air line or a hand pump; in this laboratory the hand pump has been found very satisfactory. Tubes BB′ extend through the stopper and are bent downward so that the opening may be easily accessible for closing by means of the thumb or finger. A circle of heavy copper wire is placed around the neck of the bottle and the loops extending on either side are twisted together, resulting in small eyelets on opposite sides, to one of which is loosely attached a second piece of heavy copper wire. This wire is placed over the stopper and inserted through the eyelet on the opposite side, drawn tightly, and bent sharply upward. This keeps the stopper from being forced out by the pressure and may be quickly and easily released.

To fill a buret set the stopcock C properly, close the tube B by means of the thumb, and apply the air pressure. As soon as the buret is filled the pump is stopped and the thumb instantly removed from the tube B; the excess liquid will siphon back into the bottle leaving the buret filled to the zero mark.

When a bottle becomes empty it is only necessary to raise it up until the tube AA′ clears the top of the buret; it is set on the table, the wire bent back, and the stopper containing the three tubes is removed as one piece to be inserted in a filled bottle and replaced in position for use.



[1] Received March 26, 1923.

The Potash Field in Western Texas[1,2]

By George R. Mansfield

U. S. Geological Survey, Washington, D. C.

Potash, probably of commercial quality and thickness, and at minable depth, has been found in western Texas in the Panhandle region and in adjacent territory to the south and southwest. This is no chance discovery, but the result of a definite search carried on for a dozen years by the U. S. Geological Survey with the coöperation of the Texas Bureau of Economic Geology and Technology. The search has been hampered by lack of funds, by lack of interest on the part of drillers who were in search of oil rather than potash, by the necessity of dependence upon the results of desultory wildcatting, and by the inadequacy of the methods employed in drilling for showing the quality and thickness of the potash beds encountered. Although the presence of the potash is established, definite information is still lacking regarding the thickness, quality, and extent of individual beds, the location of the richest deposits, and the place where the potash may be exploited most conveniently and cheaply.

The earlier discoveries were announced by Udden.[3] Recent information regarding these deposits has been distributed in the form of press notices, five of which have been issued by the U. S. Geological Survey beginning June 7, 1921, and in more extended papers by White[4] and Steiger.[5]

The geological conditions in western Texas resemble in many ways those of the Stassfurt district in Germany, famous for its salt and potash. In both regions "Red Beds" of Permian age—including shales, sand-stones, limestones, etc., with intercalated beds of salt, gypsum, and anhydrite—are present. The geological conditions in Texas are also similar to those in the Alsatian potash field, but the Alsatian beds are much younger. These resemblances have led geologists to expect that potash salts would sooner or later be found in Texas, especially since it has long been known that the salt beds of Texas have great thickness and it is inconceivable that everywhere throughout the salt-bearing area concentration by evaporation should have stopped short of the degree required for the precipitation of potash salts.

The geologic structure of the region, as mapped by Darton,[6] is that of a syncline or basin with axis trending nearly northeast. Darton's map, as modified by White and the author, is reproduced in part in Fig. 1. The Permian beds are not well exposed at the surface in the known potash-bearing region, so that information regarding their structure is derived chiefly from scattered wells. As data from such sources become more abundant the relatively simple basin outlined on the map will doubtless be modified by the presence of subordinate basins or folds. One basin of this type is suggested by the eastward extension in Martin and Midland counties of the area containing 400 ft. or more of salt. According to the structure indicated, the potash beds should be nearer the surface in the marginal areas of the basin and deeper toward the central part.

Earlier Discoveries of Potash

The first discovery of potash in western Texas was made in 1912 by Udden, in brine taken from a depth of about 2200 ft. in a well at Spur in Dickens County (No. 1 on map). This brine after standing was found to contain 5.4 per cent potassium calculated as chloride. In 1915 crystals of red salt in material from a depth between 875 and 925 ft. in a well at Boden in Potter County (No. 2 on map) yielded 9.2 per cent K_2O. In 1915 also, red salt from a depth between 1500 and 1700 ft. in the Miller well in Randall County (No. 3 on map) assayed 6.1 per cent K_2O, and some colorless particles from a depth greater than 1700 ft. in the same well were found to contain 10.5 per cent K_2O.

Test Boring by the U. S. Geological Survey

In the winter of 1915–16 the U. S. Geological Survey began a test boring for potash at Cliffside, six miles northwest of Amarillo in Potter County (No. 10 on map). This site was selected because it is nearly in the axis of the salt basin, near two wells from which potash has been obtained, and it is readily accessible. After interruptions through lack of funds the well was completed in 1917, at a depth of 1703 ft. Although salt beds totaling more than 350 ft. in thickness were penetrated, only insignificant amounts of potash were found in the brines and no actual potash-bearing mineral was recognized. It was thought, however, that salt beds would have been encountered for at least an additional 350 ft. had it been possible to continue drilling. Although no further test boring by the Survey has been practicable, an observer has been kept in the field to coöperate with drillers and to secure samples for analysis.

Results from Wildcatting

Since 1920 data of a more favorable nature have been accumulating as a result of observations at wildcat wells, and the mineral polyhalite ($MgSO_4.K_2SO_4.2CaSO_4.2H_2O$) has been recognized at a number of localities in an area at least 130 miles long and 80 miles or more wide. Of the seven wells that have thus far yielded information of this sort, three—namely, the Bryant well (No. 4 on map), the Burns well (No. 5), and the G. A. Jones well (No. 9)—have furnished no continuous record but only individual cuttings. These, however, show noteworthy percentages of potash. Thus, a sample taken between 2405 and 2411 ft. in the Bryant well contained 8.94 per cent K_2O in the soluble salts. In the Burns well a sample at 1780 ft. yielded 11.95 per cent of K_2O, equivalent to 21.10 per cent K_2O in the soluble salts. *Selected* pieces from cuttings between 1070 and 1075 ft. in the Jones well assayed 22.9 per cent of potash in the soluble salts. The other four wells have supplied more or less continuous records for certain depths.

Continuous Records

The River well (No. 6), the Means well (No. 7), the McDowell No. 4 (No. 8), and the St. Rita (No. 11) have furnished more nearly continuous records. These records, together with partial logs, have been plotted and placed side by side for comparison in Fig. 2. The most detailed record is afforded by the Means well, in which samples were taken every 5 ft., but all four show the occurrence of potash at more than one depth and the Means well suggests that there may be eight or ten separate potash-bearing beds in

[1] Received February 28, 1923.
[2] Published by permission of the Director, U. S. Geological Survey.
[3] University of Texas, *Bull.* **363** (1914), 82; **17** (1915).
[4] *Mining Met.*, April, 1922, 19.
[5] *Chem. Met. Eng.*, **26** (1922), 175.
[6] *U. S. Geol. Survey, Bull.* **715** (1921), 205.

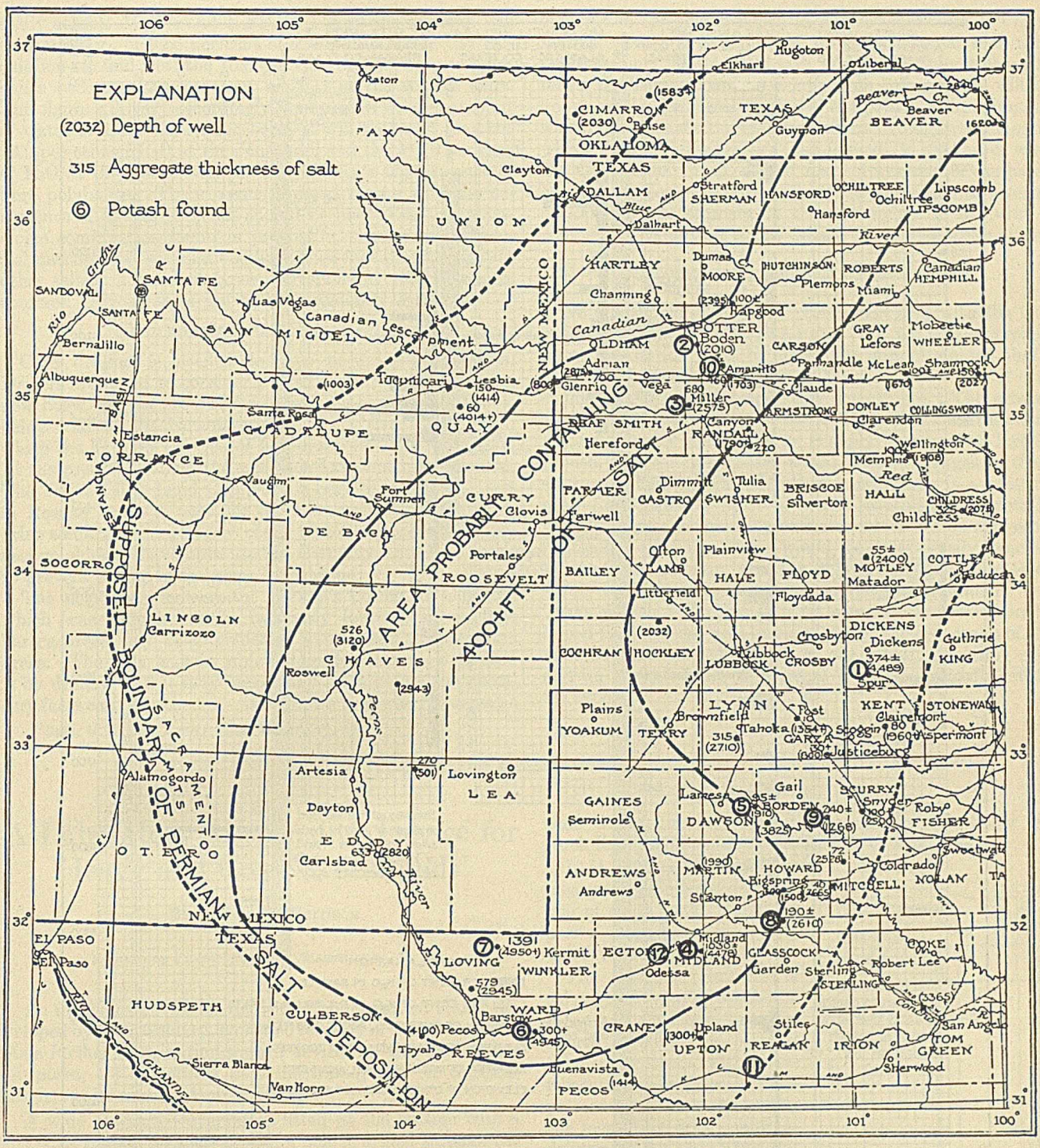


Fig. 1—Part of "Red Beds" Salt Region, Texas and New Mexico

some parts of the field. The different depths at which potash has been found in the respective wells suggest that it may occur in beds of local rather than of regional extent.

Interpretation of Results

The unsatisfactory nature of samples taken with churn drill or rotary outfits, such as were used in these wells, especially when the interval between samples is greater than 5 ft., is readily apparent. The mixture of the material effectually prevents recognition of individual beds, unless these are very thick. The dangers of salting lower beds by material from higher levels and of misinterpretation by hang-over bailings are ever present. The necessary water in the hole, by its solvent effect on salts of differing solubilities, may cause either enrichment or impoverishment of the sample, this effect being intensified or diminished by the length of time the water is in contact with the sample. The results indicated in the chart are therefore to be regarded as suggestive rather than as giving any accurate idea of the number, character, and quality of the individual beds.

The analyses recorded in Fig. 2 have been made on the arbitrary laboratory basis of 1 g. of sample to 100 cc. of water. Commercial practice may find some other proportion more suitable. According to Steiger,[5] 1 g. of polyhalite contains 0.452 g. $CaSO_4$, 0.199 g. $MgSO_4$, 0.289 g. K_2SO_4, and 0.060 g. of water. While the presence of other salts will slightly change the figures, 100 cc. of pure water at 25° C. will dissolve 0.208 g. of $CaSO_4$. This dissolved $CaSO_4$, added to the

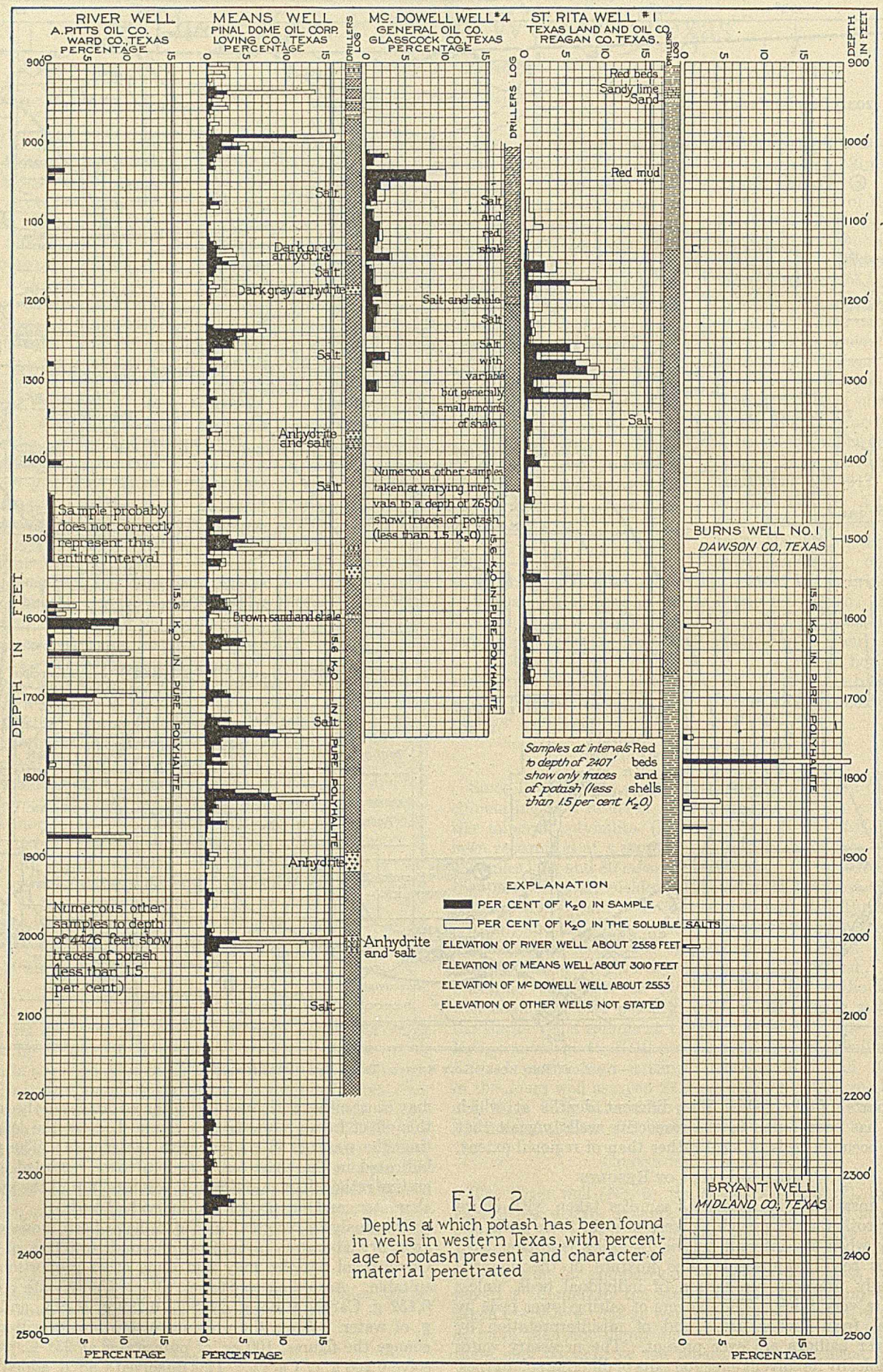


Fig 2

Depths at which potash has been found in wells in western Texas, with percentage of potash present and character of material penetrated

easily soluble $MgSO_4$ and K_2SO_4 in 1 g. of the mineral, will total 0.696 g., or 69.6 per cent of the soluble salts. By calculation we find that the 15.6 per cent of K_2O in pure polyhalite becomes 22.4 per cent of K_2O in the soluble salts. This figure will vary accordingly if a larger or smaller amount of water is used. Referring back, it will be noted that the 22.9 per cent of K_2O at the Jones well and the 21.10 per cent of K_2O at the Burns well probably indicate the presence of pure polyhalite. There seems no good reason why the occurrence of potash in Texas should be limited to the mineralogic combination found in polyhalite, though both chemical and optical examinations have thus far failed to identify other salts. Additional types corresponding with the more common German salts are to be confidently expected.

Need for Further Exploration

Core drilling is needed to give accurate information. Drillers are urged to consider potash as well as oil in sinking new holes, and to provide for coring the salt beds. This is being done at the Newnham well No. 1 (No. 12 on map) which the Farmers Oil Co., of Lancaster, Pa., is now drilling. At the present writing, the salt beds have not been reached. The Texon Oil & Land Company is beginning a similar test in Reagan County, near the St. Rita well. In such work brine solutions consisting of about 30 to 35 per cent of magnesium chloride have been used in Germany instead of water to prevent injury to the cores by solution.

The negative result at the Survey's boring at Cliffside, which was thought to be favorably located, shows that barren areas may be interspersed with possibly productive areas. The only way in which these last can be delimited is by drilling, and it may take many holes before the necessary facts can be gathered. Gale[7] notes that when systematic exploration for potash began in Alsace more than 100 deep borings were put down, 95 of which penetrated rock salt. Of these only 17 found potash layers. If this is any criterion for Texas it will be a long time before much will be known of the commercial value of the potash beds, if inquiry is confined to wildcat operations. Some far-sighted company with a view to future rather than immediate returns, or even the Government itself, should make a systematic campaign of investigation. It is believed that the evidence already obtained points strongly to the probability of deposits of commercial value and would justify the needed expenditure.

[7] Gale, *U. S. Geol. Survey, Bull.* **715** (1920), 19.

Outlook for Commercial Exploitation

No one should enter the Texas potash field with the idea of securing quick and large returns. To the cost of preliminary exploration must be added the cost of sinking shafts to depths perhaps as great as 2000 ft., and the costs of construction and labor for operating deep mines. The present market for potash is largely in the eastern and southeastern seaboard states accessible to cheaply transported foreign potash, whereas from Texas transportation charges to these states are higher. On the other hand, there is a growing need for fertilizers, most of which contain some potash, in the Central and Great Plains States, which are less accessible to foreign potash. These would be more easily reached by the Texas product. Sooner or later the demand in these states will be sufficient to support a potash industry and Texas potash will come into its own. It is greatly to be hoped that this day will be speeded, for the economics of the hour demand a rehabilitation of our rapidly depleting soils and an earnest effort to increase the amount of foodstuffs for export.

A Laboratory Dispensing Device for Heavy and Corrosive Liquids[1]

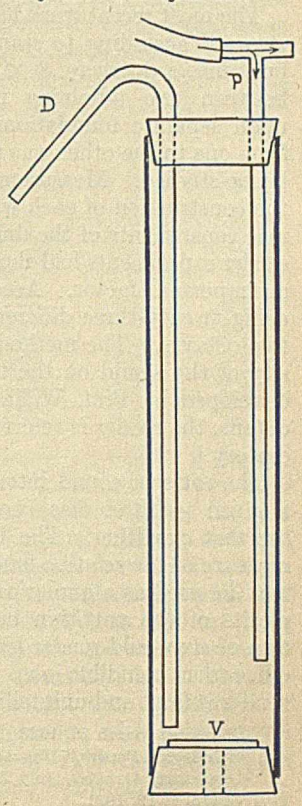
By Arthur P. Harrison

Bureau of Plant Industry, Washington, D. C.

An ingenious device for delivering concentrated alkali, developed by W. J. Geldard, appeared recently in This Journal.[2] As a further contribution toward devices for this and similar purposes, the apparatus here illustrated, now in constant use in our laboratory, is presented.

A wide graduated cylinder is fitted at the bottom with a one-hole rubber stopper, or else a hole is drilled through the flat bottom of a wide graduated cylinder, and a glass plate is allowed to rest over the hole, forming the valve V. A two-hole rubber stopper is fitted into the top of the cylinder, through which passes a delivery tube, D, reaching nearly to the bottom, and a sliding pressure tube, P, which forms a T above the stopper. One arm of the T is connected to the compressed-air line.

When the lower end of the cylinder is immersed, the liquid automatically rises in the measuring cylinder through the valve V, until it is stopped by cutting off the air outlet at the base of the pressure tube P. By holding the finger over the open arm of the T above the stopper, the compressed air forces the liquid out through the delivery tube D, at the same time closing the valve V. Upon removing the finger the stock liquid again runs automatically into the cylinder.



If it is desired to fit the measuring cylinder into a reservoir of stock liquid, it may be passed through a stopper provided with an air vent.

The desirable features of this apparatus are—regulation of quantity of liquid to be delivered, by sliding of pressure tube up or down within the measuring cylinder; compressed air is used to empty the measuring device, and, as delivery is not by siphon, the flow may be stopped instantly by removing the finger from the pressure tube if occasion should warrant; no complicated glass blowing is necessary in construction; the apparatus operates within the liquid itself, unexposed to breakage; use is not limited to a closed vessel; heavy and corrosive liquids not amenable to satisfactory manipulation by ordinary means may be easily, accurately, and speedily dispensed.

[1] Received March 16, 1923.

[2] This Journal, **15** (1923), 153.

Transmission of Sound by Standard Masonry Partitions[1]

By Paul E. Sabine

RIVERBANK LABORATORIES, GENEVA, ILL.

INVESTIGATIONS have been carried on from time to time to determine the relative merits of various types of partition walls in reducing the transmission of sound between adjacent rooms. The results obtained by different investigators have often been conflicting and, in general, the methods employed have been so different as to make direct comparisons impossible.

One of the main problems in applied acoustics at the Riverbank Laboratories has been that of determining the factors that enter into the transmission of sound from room to room by intervening partitions, and the relative importance of these factors. The earlier investigations were on simple structural units of wood, glass, and steel, such as doors and windows. These investigations showed that the heavier, and consequently stiffer, units, are more effective in reducing the intensity of the transmitted sound, but it was not possible to tell which of these physical properties was the more important. The work was then extended to flexible, porous, and inelastically compressible materials usually employed as "deadening quilts." The transmission by such materials was found to be surprisingly large, as compared with stiff, impervious wood or steel. The transmission by porous materials, such as felt, was found to be greatly reduced by the interposition of layers of impervious materials, such as building paper. It further appeared that the logarithm of the reduction of sound produced by any material of this general type increased linearly with the thickness employed. This means that each added unit of thickness reduces the transmitted energy in a constant ratio. For different materials of the same thickness, this reduction was found to follow the order of their relative densities.

The most recent work has been on masonry partitions constructed according to standard practice. These walls were built into a doorway, 8 × 6 ft., cut into an 18-in. brick wall between two adjoining rooms. These rooms were built upon separate foundations, so that transmission of sound from one to the other was necessarily by way of the partition being studied. Measurements were made at each stage in the construction of each wall, so that the effects of the separate constituents of the finished structure were known. The earlier experiments had shown that the pitch of the sound was an important factor. Accordingly, the tests were conducted using twenty-three different tones covering a total range of five octaves. The method of measuring the relative intensity of the sound on the two sides of the partition was that developed by Prof. Wallace C. Sabine.[2] For experimental details, the reader is referred to earlier articles from this laboratory.[3]

The ratio of sound intensities in two rooms separated by a given partition has been called the "reduction factor" for that partition. The logarithm of this factor is a fair measure of the relative loudness as perceived by the ear, and may be used as a numerical measure of the sound-insulating merits of the partition in question. A logarithmic reduction of six would render loud conversation in an unfurnished office room inaudible in an adjoining room; one of four would render it faint and unintelligible, but still fairly audible.

[1] Received March 16, 1923.

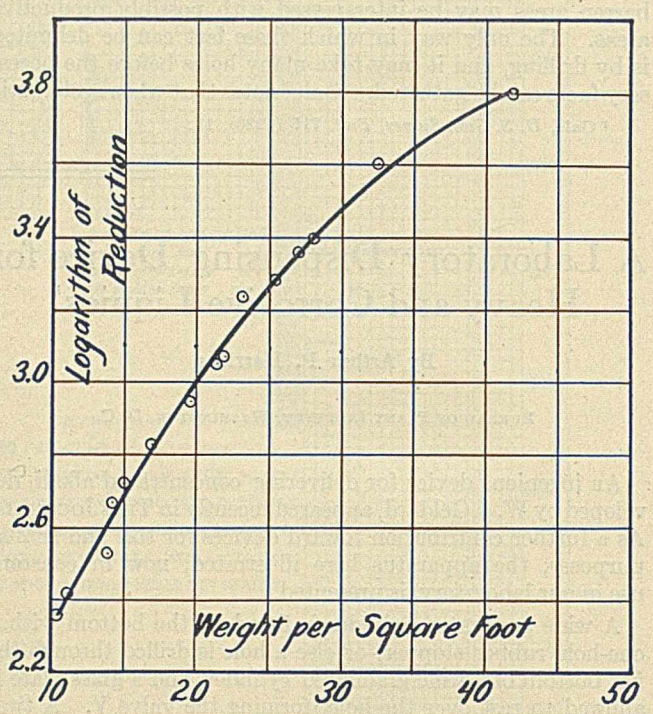
[2] "Collected Papers," Harvard University Press, 1922.

[3] *American Architect*, July 30, 1919; July 28, 1920; September 28, 1921; October 12, 1921.

The results of the tests are summarized in the accompanying table. The average logarithm of the reduction for all tones is given in the third column. In Column 4, the figures are the hydrostatic pressures over one surface of the wall measured in hundredths of a pound per square inch necessary to produce a displacement of one hundredth of an inch at the middle point. These were determined by raising the pressure in one room, which was sufficiently airtight for the purpose, above that in the other, and measuring the flexure in the wall by means of a delicate optical micrometer.

The table indicates that mass rather than stiffness is the determining factor in the general reduction of sound intensity. Sound reduction and mass per square foot follow the same order, regardless of material. On the other hand, there is no obvious correspondence between stiffness and sound reduction. For example, Nos. 8 and 14, about equally stiff, differ widely in the reduction factors, and No. 11, the stiffest wall, does not produce the greatest reduction.

The accompanying graph of the data of the table is instruc-



Tests		Average Log of Reduction	Mass per Sq. Ft.	Relative Stiffness	Average Reduction
1	2 in. gypsum unplastered	2.36	10.4	...	230
2	3 in. hollow gypsum unplastered	2.42	11.1	...	260
3	1.5 in. plaster on lath	2.53	13.9	4	340
4	3 in. solid gypsum unplastered	2.67	14.2	...	468
5	2 in. solid gypsum + 0.5 in. plaster	2.72	15.0	...	525
6	4 in. hollow clay tile unplastered	2.83	17.0	...	677
7	2 in. solid gypsum + 1 in. plaster	2.95	19.6	...	892
8	2 in. solid gypsum + 1.25 in. plaster	3.05	21.4	84	1120
9	4 in. clay tile + 0.5 in. plaster	3.07	22.0	...	1180
10	2.5 in. plaster on lath	3.24	23.2	17	1740
11	3 in. solid gypsum + 1.25 in. plaster	3.28	25.4	130	1910
12	4 in. clay tile + 1 in. plaster	3.36	27.0	...	2300
13	4 in. clay tile + 1.25 in. plaster	3.40	28.0	120	2500
14	3.5 in. plaster on lath	3.60	32.5	77	4000
15	4.5 in. plaster on lath	3.82	41.8	...	6600

tive as showing the possible degree of sound insulation that may be expected from partitions of this type. The particular material employed is clearly unimportant. Furthermore, one notes that equal increments of weight do not yield equal increments in the logarithm of the reduction, as is the case with quilt-like materials. Extrapolating the curve, it appears that for a logarithmic reduction of four a masonry wall weighing 50 lbs. per sq. ft. would be required, a figure which for cost and structural loading would be excessive in ordinary practice.

The investigation is now being extended to distinctly different types of construction.

Furfural from Corncobs[1]

I—Factors Influencing the Furfural Yield in the Steam-Digestion Process

By F. B. LaForge

Bureau of Chemistry, Washington, D. C.

The reactions involved in the production of furfural from corncobs by the steam-digestion process occur in three stages. The conversion of the pentosans into furfural does not take place quantitatively; the yield depends upon the temperature, the time, and the ratio of the amount of cobs to the amount of water employed. The optimum conditions of operation were determined in order to apply them to larger-scale investigations. These conditions are a temperature of about 180° C., a reaction period of about 2 hrs., and a ratio of cobs to water of not greater than 1:4.

SINCE the publication of the first preliminary article[2] on the production of furfural by the action of superheated water on corncobs, the work done by the Bureau of Chemistry on this subject has been extended until it has now reached the stage where the process is being put into operation on a semicommercial scale at the Color Laboratory at Arlington, Va. Before this stage was reached, however, it was necessary to determine the optimum conditions of operation by small-scale laboratory experiments.

Because of the lack of exact knowledge of the chemical nature of the corncob, the reactions involved are still imperfectly understood. It is apparent, however, that they proceed in three stages, as follows:

(1) Under the influence of superheated water the pentosans are partially hydrolyzed and changed to a condition in which they pass into solution.
(2) Hydrolysis then follows and the soluble colloidal pentosans are transformed into the sugars, largely pentoses such as xylose.
(3) The pentoses are dehydrated, yielding furfural.

$$C_5H_{10}O_5 = C_5H_4O_2 + 3H_2O$$

These stages overlap somewhat, so that some furfural is produced before complete solution of the pentosans has taken place. The conversion of pentoses into furfural does not take place quantitatively. In fact, there is a very great loss before or after the last stage of the process is complete, so that only a portion of the furfural, as indicated by the usual analytical method, is actually obtained. The maximum amount seems to be about 10 per cent, or 50 per cent of the theoretically possible yield.

The yield of furfural is dependent upon the conditions of operation in which three factors are involved—the temperature, the duration of the reaction, and the ratio of the amount of cobs employed to the quantity of water present.

For the laboratory experiments a gas-heated autoclave, provided with thermometer and outlet tube and connected with a large glass condenser, was used.[2] The distillate was measured and the furfural was determined by precipitating an aliquot portion in 400 cc. of 12 per cent hydrochloric acid by phloroglucin.[3] The results obtained were about 10 per cent too high, because of the presence in the distillate of aldehydes other than furfural, fatty bodies, and other substances that give precipitates with phloroglucin. However, since these results are used only for comparison and are those commonly given in reporting determinations of furfural and pentosans, no correction has been made.

The cobs employed were air-dried and contained from 8 to 10 per cent of moisture. Their theoretical furfural content (determined by the standard 12 per cent hydrochloric acid digestion method) was about 20 per cent, based on the air-dried weight. All furfural-yield values in this paper are based upon the air-dried weight, because that basis is the only one of importance in commercial work.

Determination of Optimum Temperature

In the experiments to determine the optimum temperature, conditions were chosen whereby practically all the furfural formed would be obtained as a distillate. In all cases 600 g. of cobs were heated with 5000 cc. of water for 45 min., after which the outlet valve was opened and the vapors were allowed to pass through the condenser at such a rate as to permit about 3000 cc. of distillate to be collected in 2 hrs. There was a variation of from 3 to 4 min. in this time, owing to the difficulty of regulating the rate of blow-off. These relations were chosen arbitrarily.

Table I—Variation in Furfural Yield with Temperature

No.	Temperature °C.	Time for Collection of 3000 Cc. Distillate Min.	Total Volume Distilled, Cc.	Furfural Concentration in Distillate % by Volume	Yield on Air-Dry Weight of Cobs %
1	155 to 157	119	3325	0.30	1.5
2	166 to 167	122	3350	1.00	5.6
3	168 to 170	108	3400	1.10	6.2
4	170 to 172	118	3400	1.24	7.0
5	172 to 175	118	3400	1.51	8.6
6	175 to 177	117	3400	1.71	9.7
7	180 to 182	117	3440	1.75	10.0
8	185 to 187	113	3440	1.68	9.7

The temperature was held constant to within 2 degrees by regulating the source of heat in each case. After 3000 cc. had been collected the flames were removed and the rate of blow-off was increased. The amount of distillate obtained after the heating had been discontinued was about 300 to 400 cc., in addition to the 3000 cc. collected during the heating period, making a total of from 3300 to 3400 cc. The whole time involved, not including that necessary to reach the temperature in question, was about $2^3/_4$ hrs. The distillate was well mixed and the furfural was determined in small, duplicate samples by precipitation with phloroglucin in hydrochloric acid. The results of eight experiments are given in Table I, and are shown graphically in Fig. 1.

[1] Received November 18, 1922.
[2] This Journal, 13 (1921), 1024.
[3] *Assoc. Official Agr. Chem. Methods*, 1920, p. 96.

The yield reached its maximum of 10 per cent at about 180° C. Very little furfural was produced at temperatures under 155° C., but the amount increased rapidly between 156° and 176° C. Above this point it remained almost constant up

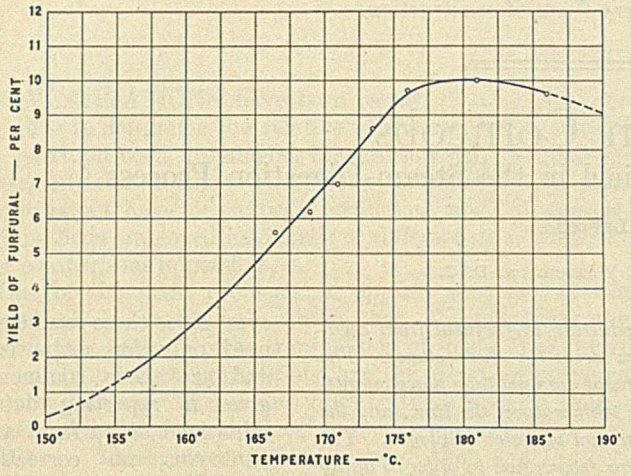


Fig. 1—Temperature–Yield Curve (Time = 165 Min. 600 G. Cobs to 5000 Cc. Water)

to 186° C. It was not convenient to go higher in the temperature scale, as leaks in the apparatus appeared at 190° C. A temperature of approximately 180° C., corresponding to about 135-lbs. gage pressure, seemed preferable.

Determination of Optimum Time

In the series of experiments here described, a temperature of 180° to 182° C. was maintained throughout the reaction period, and 1 part of cobs to 4 parts of water (1000 g. of cobs and 4000 cc. of water) were used. This ratio had been selected as the most suitable in the former work on the preparation of corncob adhesive.[4]

In the course of the process, the cobs absorb about twice their weight of water and an excess of liquid to conduct the heat and assure an even reaction must be present. By employing about 4 parts of water to 1 part of cobs the solid material is just covered with liquid during the reaction period.

In this series of eleven experiments the time was varied from 0 min. in No. 1 to 140 min. in No. 11, exclusive of the time necessary to reach the required temperature, which was from 20 to 25 min. The pressure was not noted as the autoclave used was not provided with a gage. (It must have been higher than the corresponding vapor pressure of water at the same temperatures, because of the formation of gases during the reaction. When an effort was made to work under the same conditions of temperature, using an internally heated steam digester, it was found necessary to maintain a slow blow-off throughout the process in order to avoid loss of heating efficiency due to this gas formation. A slightly higher yield is obtained, in small-scale work, by maintaining this slow blow-off. In the time-factor experiments the apparatus was kept closed until the time was up, after which the flames were removed and the pressure was relieved by blowing off the vapors through the condenser.)

The data in these experiments are given in Table II. The most important factor for practical purposes is the total amount of free furfural obtained for a given heating period. This amount, indicated by the figures in the column headed "Total Free Furfural," increases rapidly with the increase in time. The total quantity of free furfural is divided between the distillate and the liquid remaining in the autoclave. Up to a heating period of about 70 min., about two-thirds are in the distillate and one-third in the liquid. Beyond this point the proportion which appears in the distillate is higher, reaching about five-sevenths in the distillate in No. 10 and No. 11, with heating periods of 120 and 140 min. Preceding the "Total Furfural" column is one headed "Potential Furfural in Liquid," or the furfural which may be theoretically obtained by the hydrochloric acid method from undecomposed pentosans, pentoses, or other compounds present in solution. Only a part of this potential furfural may be realized as actual furfural by further heating with water. The total furfural (next to last column) is the sum of the total free furfural and the potential furfural in the liquid in the autoclave. The amount of total furfural decreases as the time of reaction increases because of the loss of some of the potential furfural during the conversion of

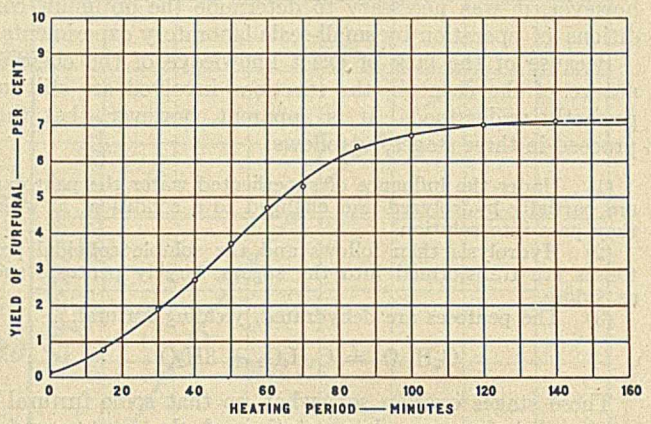


Fig. 2—Heating Period–Yield Curve (Temp. = 180° to 182° C. 1000 G. Cobs to 4000 G. Water

the pentosans to furfural. Some potential furfural remains unconverted, even after the 140-min. heating period. The results are shown graphically in Fig. 2. The optimum heating period is about 120 min.

The quantity of furfural in solution in No. 3 (116.4 g.) is about 57 per cent of the total furfural present in the cobs. At this stage, while some conversion into free furfural has

[4] *Chem. Age (N. Y.)*, 28 (1920), 332.

Table II—Effect of Time of Heating on the Formation of Furfural
(1000 g. cobs, 4000 cc. water heated at 180° to 182° C.)

		Distillate		Liquid in Autoclave						
No.	Time Min.	Furfural Concentration[a] Per cent	Free Furfural in Distillate G.	°Brix	Total Furfural in Liquid, A G.	Free Furfural in Liquid, B G.	Potential Furfural in Liquid, A–B G.	Total Free Furfural G.	Total Furfural G.	Yield of Free Furfural %
1	0	0.13	0.98	...	24.48	0.214	24.27	1.19	25.46	0.1
2	15	0.64	4.85	8.1	101.20	2.65	98.55	7.50	106.05	0.8
3	30	1.65	12.16	8.3	104.20	7.13	97.08	19.28	116.36	1.9
4	40	2.32	16.68	8.2	93.00	10.68	82.32	27.36	109.68	2.7
5	50	2.94	22.65	6.7	82.80	11.30	71.50	33.95	105.45	3.4
6	60	4.06	31.50	6.5	64.67	15.34	49.50	46.84	96.17	4.7
7	70	4.34	34.72	6.3	59.92	17.94	41.98	52.66	94.64	5.3
8	85	5.16	44.10	5.8	49.40	19.42	29.98	63.52	93.50	6.4
9	100	5.21	46.90	5.4	40.75	19.96	20.79	66.86	87.65	6.7
10	120	5.36	49.88	4.5	35.55	19.94	15.61	69.82	85.43	7.0
11	140	5.53	51.64	4.2	30.63	20.02	10.61	71.66	82.09	7.1

[a] Calculated from Kroeber's tables.

taken place, most of the dissolved pentosans, etc., have not been very much decomposed.

For approximately 50 min. simultaneous solution of furfural-giving substances and their decomposition to furfural is taking place. After heating for 50 min. there is a gradual decrease in the total furfural, owing to the progressive destruction of pentosans or furfural-yielding substances, or of furfural itself.

A certain amount of furfural-giving substances also remains in the solid residue. A consideration of the furfural content of the residues at various stages (Table III) shows that after about 70 min. practically no more furfural-yielding substances are dissolved and that the portion remaining is very resistant to the action of superheated water.

TABLE III—POTENTIAL FURFURAL IN RESIDUES FROM TIME EXPERIMENTS

No.	Amount of Washed Dry Residue G.	Potential Furfural in Residue %	Potential Furfural in Residue from 1000 G. Cob G.
1	587	13.38	78.49
2	610	9.26	55.42
4	590	4.21	24.85
6	586	3.25	19.05
9	602	2.19	13.21
9[a]	602	1.91	11.87

[a] The residue from No. 9 heated for 2 hrs. with 5000 cc. water.

The maximum yield of furfural under the conditions employed seems to be about 7 per cent, and is reached after about 2 hrs., exclusive of the time required to reach 180° C. (20 to 25 min.). Further heating adds very little to the yield; moreover, at this point a new phenomenon begins to manifest itself to a marked degree. Tarry material is deposited in such quantities as would make serious trouble in large-scale operations. It is probable that this tar results largely from dissolved substances other than pentosans which undergo deep-seated decomposition with prolonged heating.

The following experiment will illustrate this phenomenon:

A quantity of liquid obtained under the conditions of No. 10, Table II, was concentrated to remove the free furfural. The volume of concentrated liquid was 4750 cc. Five cubic centimeters gave 0.0995 g. of phloroglucin, corresponding to 51.6 g. of furfural in 4750 cc. The liquid was then heated in the autoclave for 45 min. at 180° to 182° C., after which a slow blow-off was maintained for 45 min. more with the temperature still at 180° to 182° C. After this time the flame was removed and the blow-off was completed. The volume of distillate collected was 1850 cc. Ten cubic centimeters of this distillate gave (*a*) 0.0625 g. and (*b*) 0.0650 g. of phloroglucin precipitate, corresponding to only 6.58 g. of furfural in the total distillate. Only a trace of furfural was found in the liquid remaining in the autoclave, but about 500 g. of tar had been deposited on the bottom and sides. If it were not for this complication the most economical procedure would be to discontinue the heating process after from 70 to 80 min. and use the liquid containing the furfural and dissolved pentosans for a subsequent operation. Under the circumstances, however, a cooking period of about 2 hrs. is indicated.

EFFECT OF VARYING RATIO OF AMOUNT OF COBS TO AMOUNT OF WATER

A slightly increased yield of furfural may be obtained by employing a proportion of water larger than 4 : 1. In a case where 550 g. of cobs were heated with 4500 cc. of water (1 part of cobs to 8 parts of water), the yield was 7.5 per cent for a 140-min. period and also for a 160-min. period (Table IV).

In one experiment 312 g. of cobs were employed with 5000 cc. of water (1 part of cobs to 16 parts of water), with a yield of 8.28 per cent.

Both of these ratios are disadvantageous, as the increased cost of heating the large volume of water and the distillation of the weak solution of furfural would probably more than offset the slightly increased yields (Fig. 3).

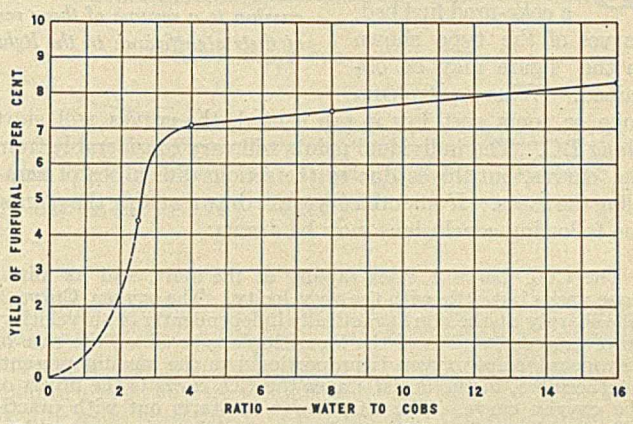


FIG. 3—WATER-COB RATIO-YIELD CURVE (TEMP. = 180° TO 182° C. TIME = 160 MIN.)

The highest yield of 10 per cent was obtained in No. 7 of the series for the determination of the optimum temperature (Table I). In this experiment the ratio of cobs to water employed was 1:8.3, and a continuous blow-off at the rate of about 25 cc. per min. was maintained for about 2 hrs. after the contents of the autoclave had been heated closed for 45 min.

It was assumed that the large yield in this case was due as much to the fact that a continuous blow-off was maintained throughout the period during which both the formation and the destruction of furfural was taking place at the most

TABLE IV—EFFECT OF VARIATION OF RATIO OF COBS TO WATER ON THE YIELD OF FURFURAL

No.	Time Min.	Ratio of Cobs to Water	Distillate: Furfural Concentration %	Distillate: Free Furfural in Distillate G.	Liquid in Autoclave: ° Brix	Liquid in Autoclave: Free Furfural in Liquid G.	Liquid in Autoclave: Potential Furfural in Liquid G.	Liquid in Autoclave: Total Free Furfural G.	Total Furfural G.	Yield of Free Furfural %
1	160	1:2.5	5.58	31.25	4.8	12.56	1.68	43.81	45.5	4.4
2	140[a]	1:4	5.53	51.46	4.2	20.02	10.61	71.48	82.09	7.1
3[b]	160	1:8	3.12	29.18 (58.00)[c]	2.5	12.19	5.32	41.37	46.69 (84.58)[c]	7.5
4	140	1:8	3.27	29.80	2.6	11.89	9.88	41.67	51.55	7.5
5	160	1:16	1.81	18.47 (59.20)[c]	1.5	7.37	0.10	25.81	25.90 (83.00)[c]	8.3

[a] These results were taken from Table II.
[b] Inasmuch as the figures in Nos. 3 and 4 of this table show no appreciable difference, it may be assumed that there would be none in the case of No. 4 if the heating period had been 20 min. longer.
[c] Values calculated to 1000 g. basis. Weight of cobs: Nos. 1 and 2, 1000 g.; Nos. 3 and 4, 550 g.; No. 5, 312 g.

TABLE V—EXPERIMENTS TO DETERMINE CAUSE OF HIGH YIELD IN NO. 7 OF TABLE I

No.	Weight of Cobs G.	Weight of Water G.	Ratio of Cobs to Water	Rate of Blow-off Cc./Min.	Concentration of Furfural in Distillate %	Weight of Furfural in Distillate G.	Concentration of Free Furfural in Liquid %	Free Furfural in Liquid G.	Total Free Furfural G.	Yield %
1	800	4000	1:5	26	2.41	62.10	0.26	3.71	65.81	8.2
2	800	4800	1:6	19	2.61	60.20	0.31	7.96	68.16	8.5
3	800	4800	1:6	27	2.29	65.40	0.27	5.44	70.84	8.9

rapid rate (Table II), as to the large proportion of water employed. This assumption was verified by three experiments (Table V).

In each experiment the heating was done with the outlet valve closed for 30 min., after which a continuous blow-off was maintained for 90 min. In each case the temperature was held within 1 degree of 180° C. for the 2 hrs., after which the flames were removed and the blow-off was completed. The yields obtained are much higher than those in any of the experiments where the autoclave was kept closed throughout the heating period, except No. 5 in Table IV. Moreover, the ratios of cobs to water employed (1:5 and 1:6) are within the range of practical application. A ratio materially higher than 1:4 is unsatisfactory, as it results in a much lower yield, which is evident from the very low yield in the case where the ratio was 1:2.5 (No. 1, Table IV).

Chemistry of Combustion in Coal-Fired Furnaces[1]

By W. K. Lewis

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The combustion reactions in the fuel bed of coal-fired furnaces have been studied by the Bureau of Mines,[2] and the following discussion is a resumé of those results, together with an interpretation of their significance in the light of certain other work in this field.

By analyzing the gases at varying points in a coke-fired fuel bed, curves of the type shown in the figure may be obtained. Where petroleum coke or some sort low in ash is used, the curves will start along BC. The individual points will vary considerably from the curves, but this is due to the serious difficulties of sampling the gases. If smooth curves are drawn among the points, the following conclusions may be drawn:

The CO_2, Curve 1, rises rapidly at the start, and its initial slope varies but little with the air velocity. The oxygen, Curve 2, falls sharply at the start practically independently of air velocity, however great, and is of the logarithmic type—i. e., the rate of disappearance of oxygen is proportional to the amount present. Furthermore, in the initial stages the CO_2 curve is the invert of the oxygen curve. The CO, Curve 3, starts out with practically no slope, rises more and more rapidly, passes through a point of inflection, and fades away to an asymptotic value. Analysis of the data will show that the slope of the CO curve at any point is proportional to the height of the CO_2 curve at the same point, and its point of inflection is, therefore, directly below the maximum of Curve 1. Finally, temperature observations prove that the temperature variation through the fuel bed is not great in any given case, and while temperature increases with increased air velocity this increase is relatively small for fuel beds of reasonable thickness. The curves as drawn are diagrammatic and not to scale.

It seems impossible to explain these facts on other than the following assumptions:

The primary reaction of carbon with air is $C + O_2 = CO_2$. The rate of this reaction is limited only by the rate of diffusion of oxygen through the stationary gas film around each particle of carbon, the rate of chemical combination of the oxygen with the carbon being indefinitely great in comparison with this diffusion. Were this not the case, the initial slopes of Curves 1 and 2 would be small at high velocities and large at low velocities, since the change in temperature of the bed with velocity is not sufficient to account for the increased reaction rate. CO is formed, not by direct combination of oxygen with carbon, but only by reduction of CO_2, as shown by the fact that its rate of formation is proportional to the CO_2 present.

Since Curve 3 is much flatter than Curves 1 and 2, it follows that the limiting factor in rate of CO formation is not diffusion but the specific rate of the chemical reaction. It therefore follows that at high air velocity the CO curve will be depressed (3*a*) and the last part of the CO_2 curve raised (1*a*). Were the fuel bed indefinitely thick, the CO_2 and CO curves would finally reach equilibrium, as indicated by the asymptotes.

Where the coke is high in ash there exists a zone of ashes, containing but little unburned combustible below the carbon itself, in which the air is largely preheated. In this case the actual curves observed are the dotted ones starting on the line OA. A striking fact, not always appreciated, is that the rate of combustion of carbon on a grate is limited solely by the amount of air forced through the grate bars, and this in turn is limited only by the air velocity that will blow the fuel off the grate. Furthermore, at a point somewhere between 3 and 6 in. practically all the oxygen in the air has been consumed, and this is true whatever the air velocity.

Explanation of Results

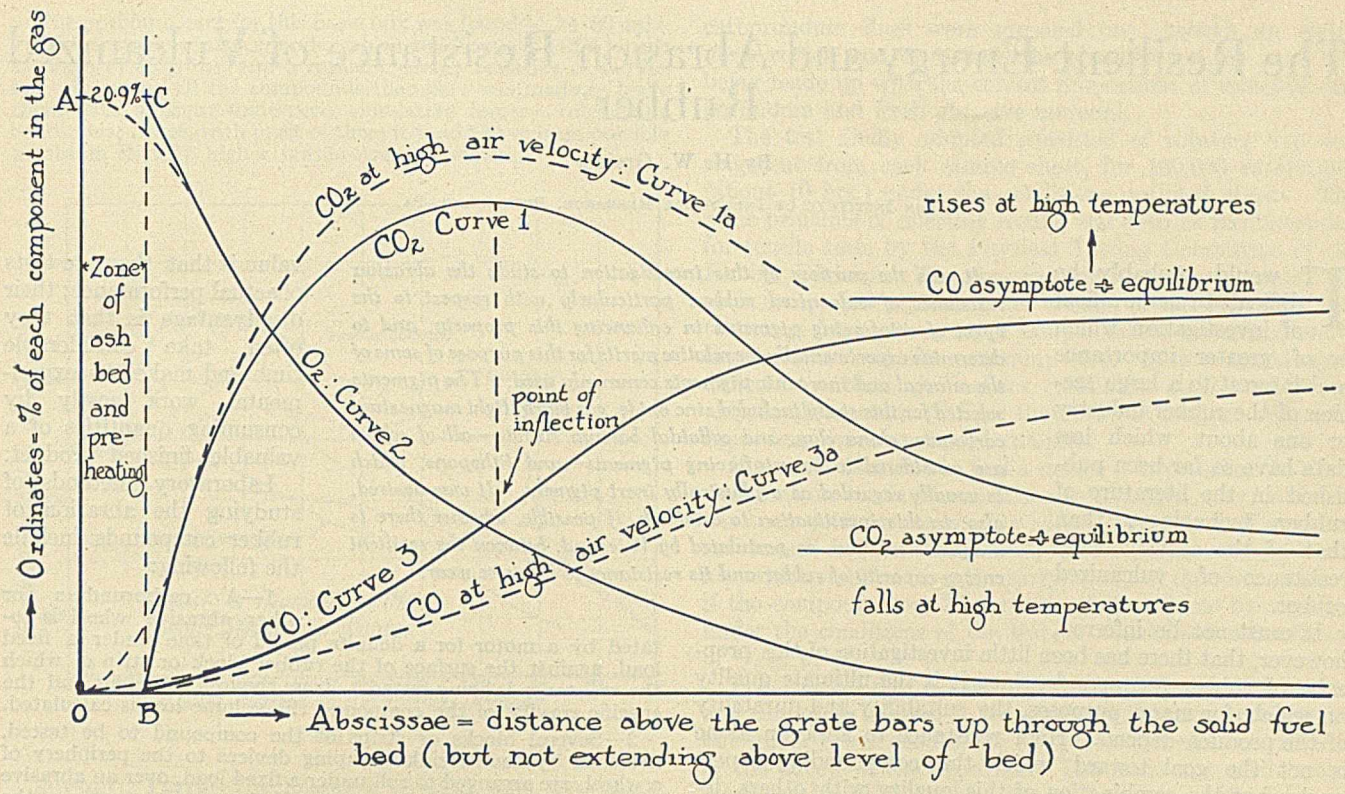
The explanation of these facts is that the rate of diffusion of oxygen through the gas film around the particles of incandescent carbon is proportional to the gas velocity, since increased velocity thins down the film. Hence, at double the air velocity twice the oxygen diffuses in and reacts, and twice the CO_2 is formed, but since there is twice the air to dilute it, the percentage composition of the gases remains unchanged. Therefore, the fuel burned per square foot of grate area per hour is proportional to the air velocity through the bed.

Since the combustion rate is proportional to air velocity, yet with formation of the same proportion of reaction products within the fuel bed, it follows that the rate of heat evolution in the bed is proportional to combustion rate; thereby, a fraction of this energy leaves the fuel bed as sensible heat in the gases; the rest is emitted by radiation, provided there is a heat-absorbing body "in sight" of the bed to take it up—e. g., the steam boiler. Since radiation increases as the fourth power of the absolute temperature, the temperature of the bed will rise only slightly to dissipate the additional heat corresponding to a great increase in combustion rate. This is why the temperature of the bed changes so little with air velocity.

Low-grade fuels may have only enough heat to raise their own products of combustion to a reasonable combustion temperature (one at which the combustion reactions progress at a reasonable rate—i. e., at least 900° C.). In such case the fuel bed must be protected from radiation, since otherwise its cooling effect will put out the fire. This can be done by keeping the bed "out of sight" of any heat-absorbing body, as in Dutch oven construction. Obviously, insulated walls, once they are brought up to furnace temperature, reflect back most of the radiation hitting them and do not cool the bed.

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

[2] Kreisinger, Ovitz, and Augustine, *Bur. Mines, Tech. Paper* **137**.



Whenever coal is burned it must first be brought to incandescence, and in this preliminary heating its volatile matter distils out and coke is left behind. The curves just referred to apply to the burning of this coke, which represents a large fraction of the combustible in the fuel. They are, therefore, controlling in furnace operation.

When coal distils it evolves unsaturated hydrocarbons of high molecular weight, and when these are heated they "crack," with deposition of carbon or soot. This is the source of most of the smoke in the combustion of coal. Bone[3] has shown that if hydrocarbons are heated in the presence of oxygen at temperatures below their ignition point, they combine with this oxygen and form additional compounds, which on further heating decompose but, even in the absence of further oxygen, without deposition of carbon. If, therefore, one wishes to avoid smoke in combustion, the coal should be distilled in a stream of air so that the hydrocarbons evolved will be formed in the presence of oxygen, to which they can add so that subsequent cracking with carbon deposition will be impossible. This can be accomplished on a hand-fired grate by firing fresh coal on a small, clear area of grate obtained by pushing back the hot coke from the fire door. The coal will be coked by heat brought to it by conduction and radiation from the surrounding fuel bed and furnace walls. The coal must never be thrown on top the hot fuel bed, because the gas rising from it is oxygen-free and coal distilled under such conditions will inevitably deposit soot in an extremely finely divided form which cannot be separated from the gas. Furthermore, this soot will burn very slowly, because if only a little air is admitted the oxygen concentration is low, while if more air is used the temperature falls, due to the dilution, to a point where combustion rate is negligible. In automatic stokers with chain or inclined grates the fuel is first heated and distilled in the presence of air, and this explains why with these stokers such high combustion rates can be realized without smoke difficulties.

[3] *J. Chem. Soc.*, **85** (1904), 1659; **87** (1905), 1248; **89** (1906), 660.

Another striking fact emphasized by these curves is that the gases leaving the fuel bed are not only deficient in oxygen, but also rich in monoxide. It is of course impracticable to operate a fuel bed with a thickness of less than 3 or 4 in., and usually more is required. Consequently, the fraction of the total carbon leaving the fuel bed in the form of CO is large, and there is not enough oxygen with it to burn it. Furthermore, the hydrocarbons formed on distillation of the fuel must also have further oxygen mixed with them to insure complete combustion. Since this additional oxygen cannot possibly come through the fuel bed, it is absolutely necessary to admit it as secondary air. Since excess air represents a serious heat loss up the stack, this secondary air should be kept a minimum. On the other hand, the oxidation of these gaseous products of primary combustion and distillation is purely a gas reaction and relatively slow. Outstanding problems of furnace design and operation are, therefore, the admission of the right amount of secondary air, mixing this secondary air perfectly and quickly with the gaseous products of primary combustion, provision of adequate combustion space and, where possible, of hot catalytic surfaces to insure completion of the oxidation reactions. The main reason why oil-fired furnaces have a higher thermal efficiency than coal-fired ones is the greater ease of securing in them perfect mixing of the air supply with the gaseous products of primary combustion and distillation, thus enabling the operator to reduce excess air.

The problems of combustion are satisfactorily met in the best modern boiler furnaces, in the construction and operation of which practice is well standardized. On the other hand, in most chemical furnaces important special conditions obtain which make these problems exceedingly difficult for the chemical engineer. Furthermore, unlike boiler practice, these special factors vary widely in different industries and operations. To solve them, therefore, requires a peculiarly thorough appreciation of the fundamental facts outlined above, that provision may be made to meet the conditions necessary for efficient combustion.

The Resilient Energy and Abrasion Resistance of Vulcanized Rubber[1,2]

By H. W. Greider

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It was the purpose of this investigation to study the abrasion resistance of vulcanized rubber, particularly with respect to the effect of reinforcing pigments in enhancing this property, and to determine experimentally the relative merits for this purpose of some of the mineral and inorganic pigments commonly used. The pigments selected for this study included zinc oxide, gas black, light magnesium carbonate, china clay, and colloidal barium sulfate—all of which are considered to be reinforcing pigments—and lithopone, which is usually regarded as a physically inert pigment. It was desired, also, in this investigation to establish, if possible, whether there is a definite relation, as postulated by Wiegand, between the resilient energy capacity of rubber and its resistance to abrasive wear.

It would probably be difficult to name a field of investigation which is of greater importance and interest to a large section of the rubber industry or one about which less data have so far been published in the literature of rubber technology, than that of the abrasive-wear resistance of vulcanized rubber.

It must not be inferred, however, that there has been little investigation of this property of rubber compounds, since it is the ultimate quality on which, for many purposes, the suitability and durability of the product depend. High resistance to abrasion alone is not the goal toward which the compounding expert works, but the combination of this quality with others desirable in the finished product—such as high tensile strength, resilience, endurance of repeated flexing, and relatively low permanent set—determines the composition of the compound and the technic of its manufacture for such extended uses as motor-tire treads, rubber belting, and rubber footwear. The proper combination of such qualities for a particular purpose is commonly designated as "toughness."

In a recent paper on the properties of rubber compounded with mineral rubber, North[3] gave data showing the abrasion losses for a number of samples containing various proportions of that compounding ingredient. His results showed that increasing proportions of mineral rubber produced corresponding decreases in the abrasion resistance of the compounds. This appears to be the only actual information regarding this property of rubber published to date. Wiegand,[4] however, studied the effects of various compounding ingredients upon the stress-strain curve of rubber and upon its resilient, energy capacity. He advocated the adoption of the total resilient-energy capacity (work) of vulcanized compounds as a numerical measure of the reinforcing or toughening action of the pigments used in compounding them.

Methods of Determining Resistance to Abrasion

The practical method of testing the abrasive-wear resistance of rubber products is that in which the compound in its finished form is subjected either to actual service conditions or to conditions which simulate them very closely, as in the cases where tires are run on a test car until the tread wears through. Such tests can hardly be called laboratory tests, although most rubber companies make them as a regular part of their development work. Their greatest value is that they are tests of actual performance; their disadvantage is that they often take considerable time and make the experimental work costly by consuming quantities of a valuable finished product.

Laboratory methods of studying the abrasion of rubber compounds include the following:

1—A carborundum or other abrasive wheel is rotated by a motor for a definite period of time under a fixed load, against the surface of the rubber block or strip of which the resistance is being tested. From the loss in weight and the specific gravity of the compound the volume loss is calculated.

2—Several blocks or strips of the compound to be tested, attached by countersink clamping devices to the periphery of a wheel, are arranged to roll under a fixed load, over an abrasive surface. From the loss in weight and the specific gravity of the compound the volume loss sustained during a stated number of revolutions under the conditions of the test is calculated. Except for the accelerated character of the abrasion this approaches an actual performance test, but clogging of the abrasive surface makes the results difficult to check. This type of machine, which was developed at the Bureau of Standards by Hart and Bowker[5] for studying the abrasive wear of leather, combines in one test the effect of the abrasive and a shearing action due to driving under load over the abrasive surface.

3—Circular rings (inner diameter, 1.75 in.; outer diameter, 2.25 in.), stamped by means of a steel die from a sheet of the rubber compound about 0.125 in. thick, are carefully weighed and placed between steel separator rings on a steel spool and clamped in position so that about two-thirds of the surface of each ring are exposed to the action of the abrasive. The spool is attached to a vertical spindle, and is rotated in a granular, loose, abrasive material. After a certain number of revolutions the rings are removed, carefully cleaned, and weighed. The loss in weight are calculated to percentage volume loss of the compound, under the conditions established for the test. The method is that of Sproull and Evans.[6]

Experimental Method

Six series of rubber samples were prepared, in the basic mix described below, to obtain the data upon which this paper is based. With each of the six pigments—zinc oxide, gas black, light magnesium carbonate, china clay, colloidal barium sulfate, and lithopone—compounds were prepared containing varying proportions by volume of the pigment from zero, represented by the basic mix, up to 30 volumes to each 100 volumes of rubber in the compound.

Basic Mix—The basic mix used in the preparation of all the compounds studied in this investigation had the following composition:

	Weight Ratio	Volume Ratio
Pale crepe rubber	50	50
Smoked sheet rubber	50	50
Zinc oxide	5	0.8
Sulfur	5	2.4
Hexamethylenetetramine	1	0.8

[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] The data on which this paper is based were obtained in the course of an investigation of the effect of light magnesium carbonate on the abrasive-wear resistance of rubber, conducted for the Magnesia Association of America, at the Mellon Institute of Industrial Research of the University of Pittsburgh.

[3] *Chem. Met. Eng.*, **26** (1922), 254.

[4] *Can. Chem. J.*, **4** (1920), 160; This Journal, **13** (1921), 118.

[5] *Bur. Standards, Tech. Paper* **147** (1919).

[6] Paper read in part by Dr. Fisher before the Division of Rubber Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 3 to 7, 1921.

The optimum cure for this basic mix was found to be 80 min. at 50 lbs. steam pressure, under which conditions it had a tensile strength of 3230 lbs. and a resilient energy capacity of 440 ft.-lbs. In curing all the compounds the effort was made to leave them with a slight undercure, simulating factory vulcanizing conditions; hence, with most of them it would have been possible to obtain slightly higher tensile-strength values.

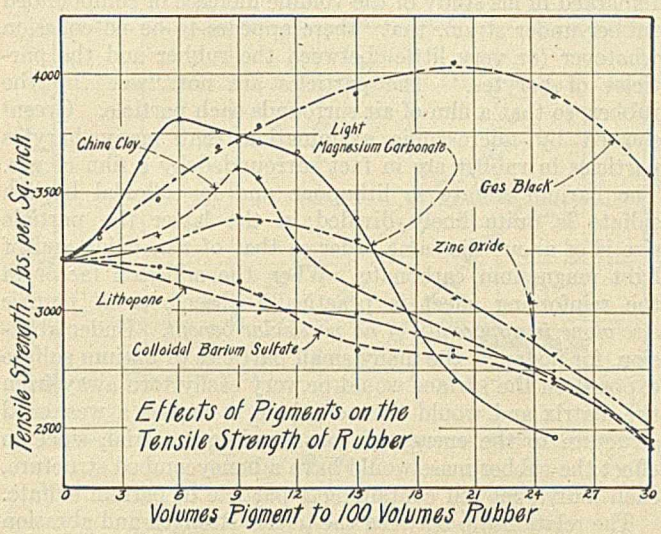

Fig. 1

Physical Tests—The following physical tests were made, following approved methods, upon all the samples discussed in this paper: tensile strength, ultimate elongation, hardness (durometer), total resilient-energy capacity, and rigidity.

Rigidity values for the samples, as measured by the tensile stress required to produce a 300 per cent elongation, were obtained directly from the stress-strain curves. Vogt[7] has suggested that the slope of the line representing rigidity values for successive increments of filler is a measure of the reinforcing effect of the pigment.

Method of Abrasion Tests

After considering the various possible methods of studying abrasion, the one most likely to give accurate and consistent results in such an experimental study seemed to be that of Sproull and Evans.[6] An advantage it possesses which is of great importance in this work is that the test rings for the abrasion-loss determination and the test strips for the determination of tensile strength, elongation, resilient energy, rigidity, and hardness are all cut from the same sheet.

In order to obtain consistent results in the determination of abrasion-resistance values, it was found necessary to adhere to rather rigid conditions in the carrying out of the test. In the method outlined by Sproull and Evans, recourse was had to the use of a "standard" compound, one for which the abrasion-resisting qualities in actual use were known; and the results of every test were calculated to an index number, using the value for this compound as 1000. This enabled them to ignore the effects of slight variations in the speed of the machine, and differences in temperature and in the grain size of the abrasive. Since in this investigation no compound of standard abrasion performance was available, it was found necessary to standardize the test itself somewhat further. All tests were run at a constant speed of 170 revolutions per minute, or about 10,000 revolutions per hour, under which conditions the abrasive and samples heat up to about 150° F. (65.5° C.). Unless the grain size of the abrasive was the same for each test the abrasion results could not be duplicated on the same sample. The abrasive used was granular carborundum designated as Grain C, Stock T. After each test all the rubber dust and carborundum fines were screened out through an eight-mesh screen and discarded, the abrasive for the next test being made up with the correct proportions of screened carborundum and fresh abrasive material.

The test finally adopted consisted of rotating five test rings cut from each sample sheet, for 100,000 revolutions (about 10 hrs.) under the conditions outlined above. The same principle of selecting results was used as recommended for tensile tests by the Physical Testing Committee of the Rubber Division. The abrasion results finally accepted for each compound represent the *average* of not less than five test rings from one or more sample sheets vulcanized under the conditions of the optimum cure. It was found more difficult to obtain good check results for stocks containing only small amounts of filler than for the tougher and more rigid, heavily compounded samples.

It seemed desirable to find a means of expressing the abrasion data in terms of resistance to abrasive wear, and this has been done by designating as the "coefficient of abrasion resistance" for each compound, the reciprocal of the volume loss which resulted from the carrying out of the test. Hence, if the compound lost 20 per cent of its volume by abrasion under the conditions of the test, it would have a coefficient of $^1/_{0.20}$, or 5.

The "coefficients" obtained have no absolute or fixed value, and cannot be referred to the results of abrasion tests carried out under other conditions, except for general comparisons of the effects of the pigments. The basic mix used in this work was found, from the average of a large number of tests, to lose 10.3 per cent of its volume as a result of accelerated abrasion under these conditions, and has, therefore, as a "coefficient of abrasion resistance," the value 9.7.

Discussion of Abrasion-Resistance Data

The curves of Fig. 1 represent the tensile-strength data for all the compounds prepared with the six pigments studied. The highest breaking-load figures are given by gas-black stocks, followed by light magnesium carbonate, china clay, and zinc oxide, in the order named. These four pigments

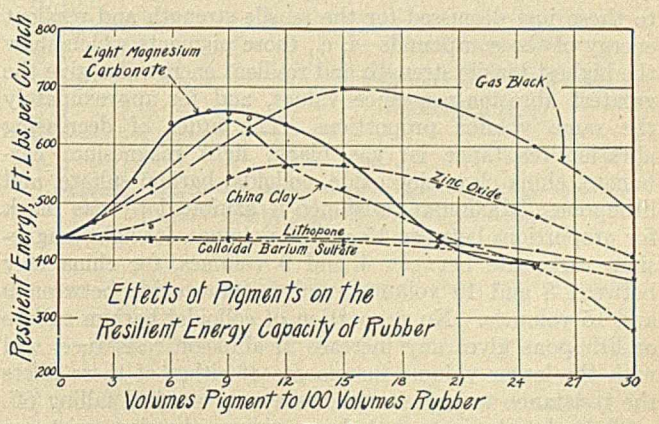

Fig. 2

all give tensile strength above that of the basic mix for certain compounding ranges, whereas lithopone and colloidal barium sulfate do not give increased tensile strength in any proportion. The tensile-strength values obtained are higher than would be given by the same reinforcing pigments in unaccelerated mixes.

Resilient-energy capacities for these compounds are represented by the curves of Fig. 2. They resemble the tensile-strength curves just discussed, in that they rise to maxima at approximately the same volume proportions for gas black, magnesium carbonate, zinc oxide, and china clay, although the curves are not identical in their trend. Lithopone and

[7] *India Rubber World*, 66 (1922), 349.

colloidal barium sulfate show quite unusual resilient-energy behavior. Although any addition of either of these pigments gives lower tensile strength than that of the basic mix, the resilient-energy capacity is equal to that of the basic mix until more than 10 volumes of the pigment have been incorporated. Neither, however, gives any increase in re-

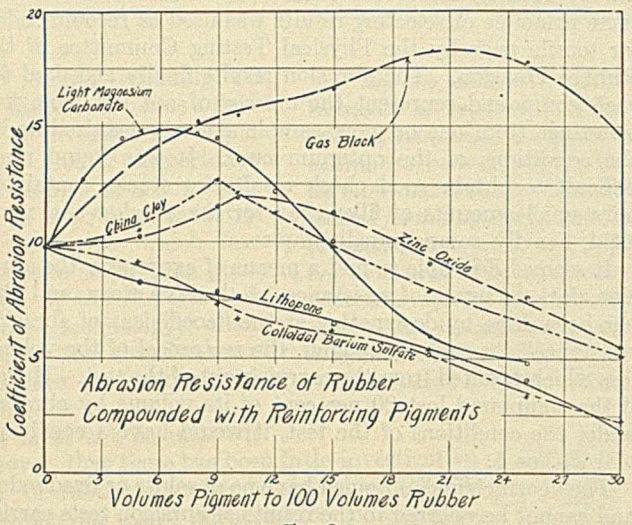

FIG. 3

silient energy for any volume proportion, and *they are not, therefore, in the strict sense reinforcing pigments.* The maximum resilient-energy capacity for gas-black compounds is given by proportions between 15 and 25 volumes, for magnesium carbonate between 6 and 12 volumes, for china clay between 8 and 10 volumes, and for zinc oxide between 10 and 20 volumes; the order in which these pigments increase the resilient energy being the same as given above for tensile strength.

On examining the curves showing the abrasion-resistance values for these pigments (Fig. 3), it is immediately apparent that there is a general similarity in the trend of the curves to those just discussed for the tensile strength and resilient energy of the compounds—i. e., those pigments which show the highest tensile strength and resilient energy also give the greatest abrasion-resistance values, and for approximately the same volume proportions. The order of decreasing abrasion resistance is: gas black, light magnesium carbonate, china clay, zinc oxide, colloidal barium sulfate, and lithopone. Maximum resistance is exhibited by gas black for proportions between 15 and 25 volumes, for light magnesium carbonate between 4 and 9 volumes, for china clay between 8 and 10 volumes, and for zinc oxide between 9 and 15 volumes. No proportion of colloidal barium sulfate or lithopone gives any increase in abrasion resistance, and with the larger volume increments of either of these fillers the resistance to abrasion shows a very marked falling off.

These data indicate that the maximum abrasion resistance given by gas black (at 20 volumes) is 88 per cent greater than that of the basic mix, while at the maximum for magnesium carbonate (6 to 8 volumes) it is 52 per cent greater. For china clay the increase at the maximum (9 volumes) is 30 per cent, and for zinc oxide (at 10 volumes) the increase is 24 per cent. When these pigments are to be used for their *abrasion-resistance qualities alone,* they should evidently not be incorporated in proportions greater than those indicated above, *assuming that these data represent correctly the actual abrasion performance of compounds containing these pigments.*

The inferior abrasion resistance given by rubber samples compounded with lithopone and with colloidal barium sulfate seems to demand a special explanation, since both these pigments show, in proportions up to 10 volumes, resilient energy calculated from the stress-strain relations equal to that of the basic mix. In these two cases resilient energy is evidently no index of resistance to abrasion. The explanation lies apparently in the fact that barium sulfate does not have a high specific adhesion to the rubber matrix. Schippel[8] remarked in his study of the volume increase of compounded rubber under strain, that "there appears to be no cohesion whatever (or very little) between the rubber and the particles of barytes." The particles are not "wet" by the rubber, so that a film of air surrounds each particle. Green[9] showed by microscopic examination that many barytes particles in rubber are in fact surrounded by a film of gas. The barium sulfate in lithopone and in colloidal barium sulfate is quite finely divided; in the latter the particle size is of about the same order as that of zinc oxide and of light magnesium carbonate. When the adhesion factor in the reinforcing effect is practically absent, *small particle size alone is apparently of no particular benefit.* Under abrasion, for instance, the many small particles of barium sulfate exposed on the surface would be very easily torn away from the matrix and would then continue to expose a weakened structure to the energy of the abrading material, since in effect the rubber mass would have a honeycombed structure, each individual cell containing a particle of barium sulfate.

The relationship between the tensile strength and abrasion resistance of rubber is shown in Fig. 4. It is evident that, while increasing tensile strength accompanies increasing abrasion resistance, there is not a direct proportionality between the two properties. Also, there is a very marked difference between the results obtained with the true reinforcing pigments—gas black, zinc oxide, magnesium carbonate, and china clay—and those given by lithopone and colloidal barium sulfate. The abrasion resistance with the last two fillers decreases more rapidly with decreasing tensile strength

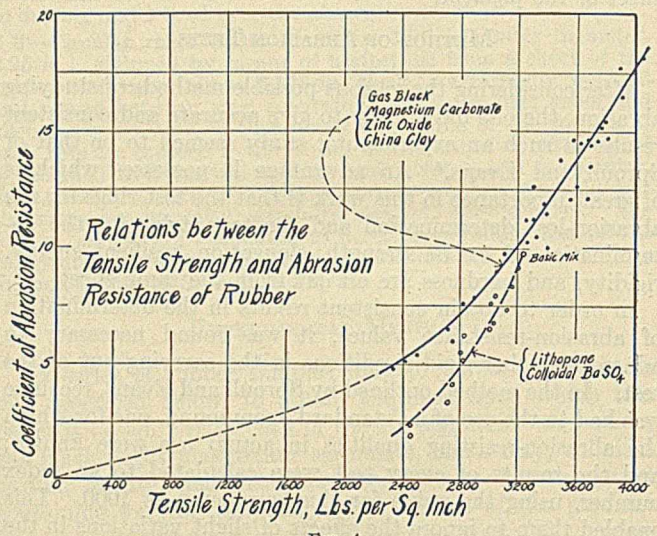

FIG. 4

than with the four first-named pigments, and with no proportion of filler is it greater than that of the basic mix. For tensile strength above 3600 lbs. per sq. in. the rate of increase of abrasion resistance with increasing tensile strength is quite rapid, suggesting that rubber cured with certain very rapid accelerators to give even higher tensile strength, and compounded with reinforcing pigments, should give exceptionally high resistance to abrasion.

The values for tensile product and abrasion resistance plotted in Fig. 5 indicate that there is no significant relation-

[8] THIS JOURNAL, 12 (1920), 33.
[9] *Ibid.*, 13 (1921), 1029.

ship between the two properties. Tensile product therefore, can hardly be considered a satisfactory device for evaluating the toughness of compounded rubber.

In Fig. 6 resilient-energy values have been plotted as abscissas, and the corresponding coefficients of abrasion resistance as ordinates, for gas black, magnesium carbonate, zinc oxide, and china clay. These data do not show an exact

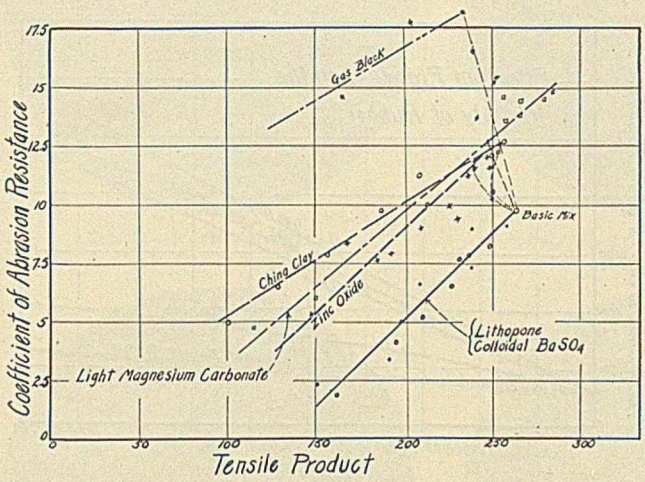

Fig. 5

proportionality between abrasion resistance and resilient energy, although, in general, compounds which have high resilient energy also have high abrasion resistance. A line has been drawn through the origin and the point representing the basic mix, to show the deviations. Some compounds, represented by points above that line, have greater abrasion resistance than would be indicated by their resilient energy; these compounds contain gas black or magnesium carbonate. Many other compounds fall below the line, having less abrasion resistance than would accord with their resilient-energy values; these are mostly compounds containing zinc oxide or china clay. If then, resilient energy alone is an insufficient index of the abrasive wear resistance of these compounds, it is pertinent to examine the other physical properties to determine in what other respects gas black and magnesium carbonate differ from zinc oxide and china clay in their effect on rubber. First, they impart higher tensile strength, and second, they give greater hardness (or rigidity). The divergence from a direct proportionality to resilient energy seems too great in many cases to be explained entirely on the basis of the higher tensile strength, especially since the latter usually accompanies high resilient energy; and this makes it appear probable that hardness or rigidity is the principal other factor.

If the foregoing postulation is correct, then, for the four pigments named, the maximum toughness as measured by abrasion resistance for each pigment should be found at that volume concentration at which the product of resilient energy and hardness is a maximum. This is suggested further by the fact that, while such physical properties as tensile strength, tensile product, and resilient energy, used in the evaluation of rubber, rise to a maximum value at a definite volume concentration for each pigment and then fall off with further successive increments, there are two properties, hardness and rigidity, which show linear increases with successive additions of pigment in the compound.

That there is an *approximate proportionality* between the abrasion resistance at the point of maximum reinforcement and the product of resilient energy and hardness, for the four reinforcing pigments studied, is shown by Fig. 7. It should be noted, however, that the compound giving the maximum product for each pigment is not identical in every case with the compound giving the maximum abrasion resistance in this test. All the points, however, fall near enough to the line to confirm the apparent relationship. From the data available, it has not been found possible to show that such a relationship holds, with even approximate exactness, for proportions of these pigments greater or less than required for maximum reinforcement. This will evidently require further and more precise study.

The point representing the basic mix does not fall upon the line, but its abrasion resistance as determined by this test is greater than would be indicated by the product of resilient energy and hardness, suggesting that this type of abrasion test gives results for abrasion resistance which are slightly too high for pure gum or lightly compounded stocks, and that the actual abrasion resistance of the basic mix and of the lightly compounded samples is not quite as great as represented in Fig. 3, while that of the more rigid compounds is relatively greater. Since the test is carried out with a loose, granular abrasive, the effect of shear due to load on the rubber surface is small. There can be no doubt that the pressure between the rubber and the abrasive surface and the angle at which they meet will have some influence on abrasion loss.

Since the process of abrasion in rubber consists of the continual tearing away of small masses of rubber or of pigment particles from the rubber matrix, it will be appreciated that any physical characteristic of the rubber which renders this tearing away more difficult will increase the abrasion resistance. When a worn rubber article—as, for example a tire tread—is examined under a low magnification (50 to 100 diameters), it is observed that in addition to many rela-

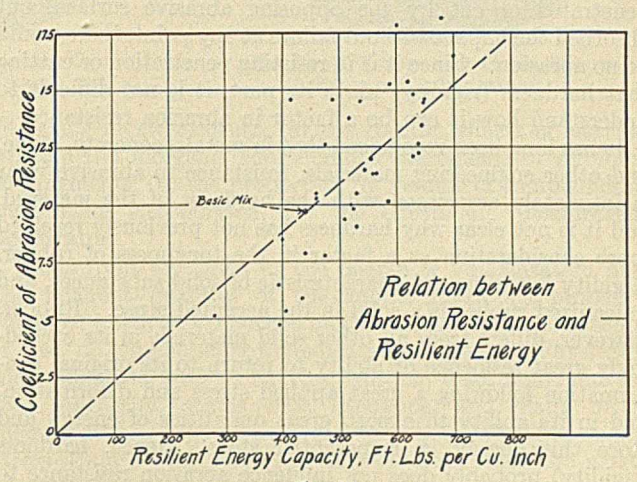

Fig. 6

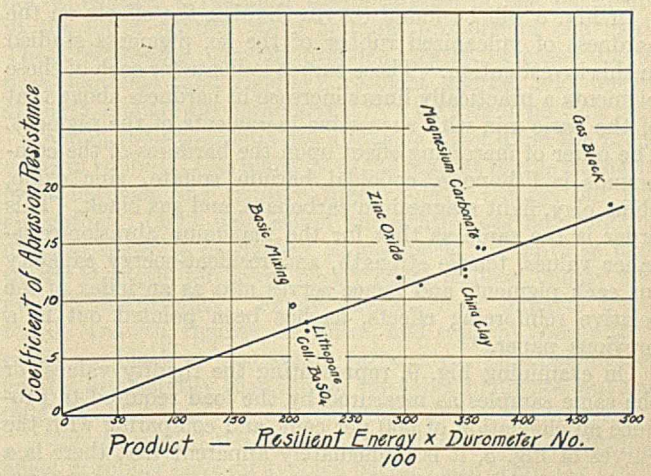

Fig. 7

tively deep cuts and scratches the surface contains innumerable pits of irregular form. (Figs. 11 to 17.) These pits have been produced by the tearing out of relatively larger masses of rubber, and the walls and edges of the pits present to the abrading forces many smaller masses already partly exposed, so that the application of a relatively small amount of energy at a definite angle against the surface of one of these

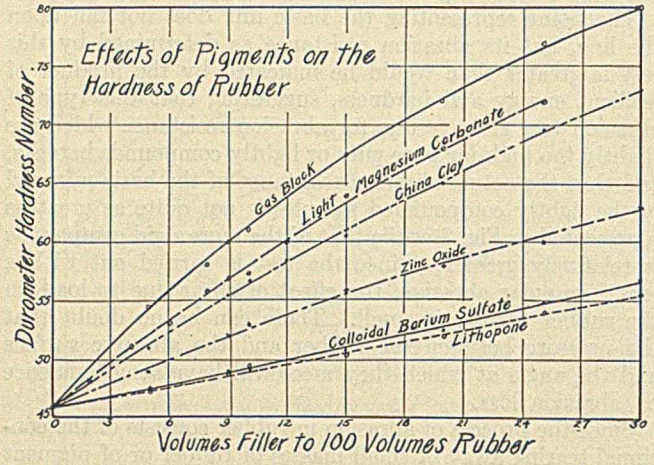

Fig. 8

small masses will cause it to be torn away from the larger mass. In the mechanism of the abrasion process a portion of the surface must be cut or penetrated before any of the rubber can be gouged away—i. e., if the surface had such perfect elasticity or hardness that it could not be easily penetrated or cut by the opposing abrasive surface, but absorbed the impact without failure at any point, there would be no abrasion. Since it is in resisting penetration or cutting that hardness (rigidity) plays its part, it is not difficult to understand how it can be a factor in abrasion resistance.

It has long been recognized that in metals, concrete, stone, and other engineering materials, resistance to abrasive wear is intimately associated with the hardness of the material, and it is not clear why hardness has not previously received more consideration as a factor in the toughness of rubber. Rigidity is the special characteristic of solid substances, and vulcanized rubber is a solid in the accepted sense. Rubber, however, differs from all other solid materials in its exceedingly great resilience or ability to return to its original conformation following a great applied stress and deformation, and in its ability to absorb great quantities of energy and store this energy in a potential state. Hence, hardness (rigidity) probably does not influence abrasion resistance to as pronounced a degree as with less elastic materials.

In Fig. 8 will be found curves showing the effects on the hardness of vulcanized rubber of the six pigments studied in this investigation. These curves indicate for each of these pigments a practically linear increase in hardness above that of the basic mix with successive increments of the pigment. The order of increasing effect upon the hardness of the compounds is lithopone, colloidal barium sulfate, zinc oxide, china clay, light magnesium carbonate, and gas black. This order is the same as that for the maximum abrasion-resistance values, tensile strength, and resilient-energy capacity for each pigment, and hence serves also as an index of the relative reinforcing effects, as has been pointed out in a previous paper.[10]

On examining Fig. 9, representing the rigidity values for the same samples as measured by the load required to produce an elongation of 300 per cent, and comparing with the curves of Fig. 8, it is immediately apparent that there is a very striking similarity between these curves and those for hardness. The rigidity curves are also very nearly linear and lie in almost exactly the same relative positions as those for hardness. The order of increasing rigidity for the six pigments studied is the same as for their effects on hardness. While rigidity and hardness can scarcely be considered identical physical properties, it seems certain from the data

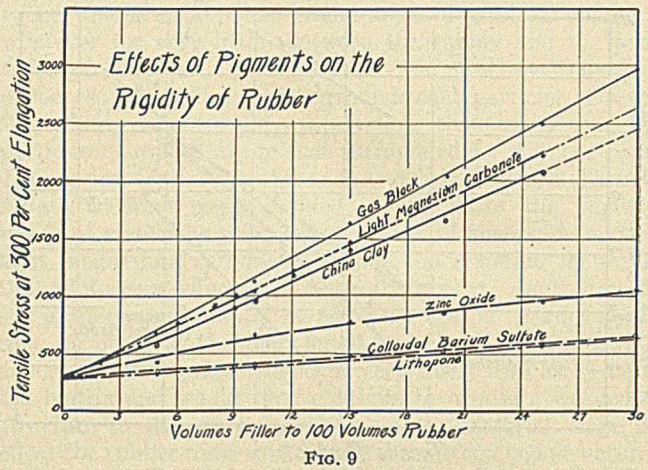

Fig. 9

here presented, that they must be, at least with approximate accuracy, parallel functions of the proportion by volume of filler added, regardless of whether the filler is a true reinforcing pigment or not.

Hardness is usually considered as resistance to penetration or indentation, and methods for measuring the hardness of rubber involve the indentation of the rubber surface by a blunt or rounded point (durometer or densimeter), or by a spherical steel ball (plastometer), under load. Gurney[11] found that in the case of the durometer—with which the hardness tests were made, an instrument in which the indenting point has a fixed diameter and length and operates against a fixed power in the spring—the force in dynes and the linear displacement of the point are both approximately proportional to the "durometer number" read on the instrument.

Rigidity, or stiffness, is correctly expressed as the specific resistance to stress, either tensile or compression, and is measured by the stress load required to produce a stated extension of the material. Although the method of measur-

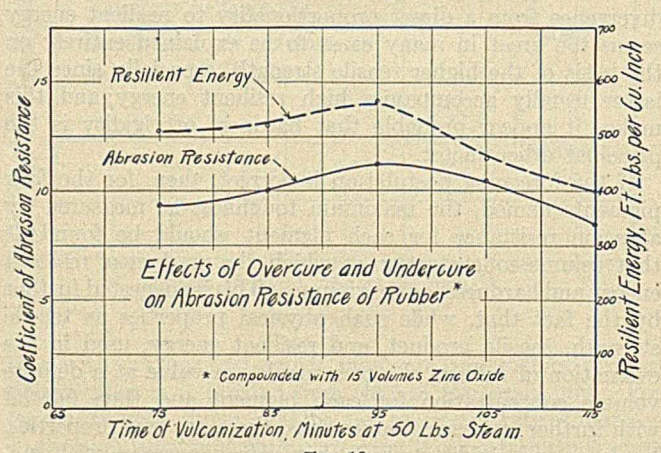

Fig. 10

ing this quality is different from the measurement of hardness, both qualities seem to involve the same "inner property" in the rubber network, since rubber under stress not only becomes more resistant to increasing loads, but also becomes very much harder, as measured by resistance to penetration.

[10] This Journal, 14 (1922), 385.

[11] This Journal, 13 (1921), 707.

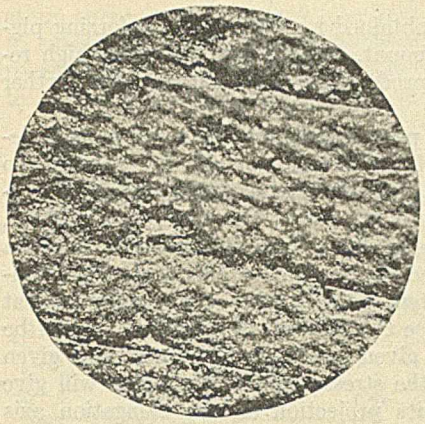

Fig. 11—Worn Tire Tread (50 Diameters)

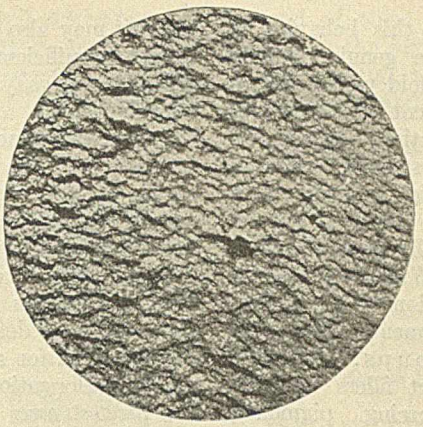

Fig. 12—20 Volumes Gas Black (50 Diameters)

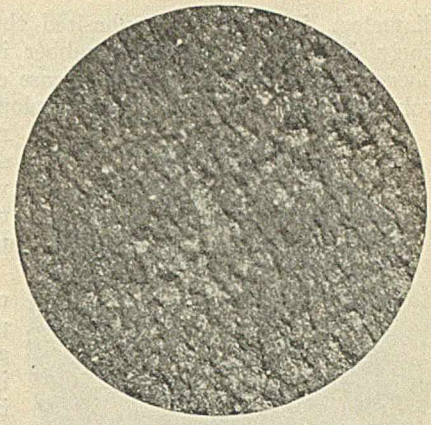

Fig. 13—8 Volumes Magnesium Carbonate (50 Diameters)

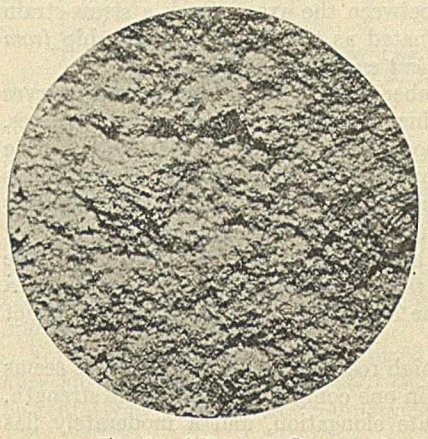

Fig. 14—9 Volumes Clay (50 Diameters)

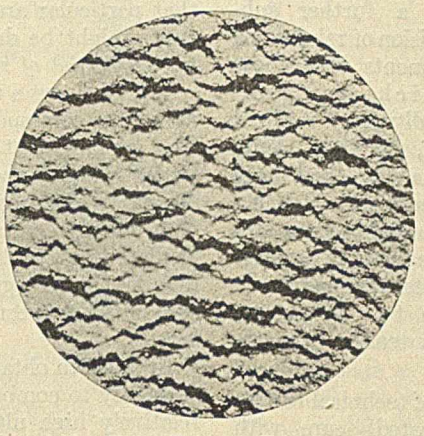

Fig. 15—10 Volumes Zinc Oxide (50 Diameters)

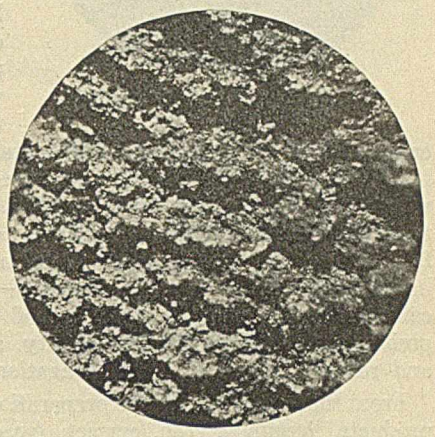

Fig. 16—10 Volumes Colloidal Barium Sulfate (50 Diameters)

In Fig. 10 typical results are given showing the effects of overcure and of undercure on the abrasion resistance and resilient energy of a sample compounded with 15 volumes zinc oxide. It will be observed that the maximum for both resilient energy and abrasion resistance is reached at the same state of cure, although the curves do not exactly parallel each other. The data confirm the observation of Schidrowitz and Burnand,[12] that overcured rubber is *rigid rather than tough.*

The appearance of the test rings following the abrasion-loss determinations is shown in Figs. 12 to 17, inclusive, the flat surface of each ring having been photographed at 50 diameters magnification, to show the relative degree of wear with each of the pigments studied. Fig. 11 represents a photomicrograph at the same magnification of a worn tire tread. Aside from the cuts in the surface, the character of the abrasion is somewhat similar to that in this laboratory test. The large number of small cuts in the surface of the worn tread suggest that in actual service hardness (rigidity) may be of greater importance in resisting wear than in this test, where such cuts are almost entirely absent.

Factors Influencing Stress-Strain Relationships of Rubber

Abrasion resistance, like many other mechanical properties of rubber, seems to depend to a considerable degree upon the stress-strain relationships of the vulcanizate. The factors which determine the position of the stress-strain curve, its degree of curvature, and its angle of inclination to the stress axis, include (1) the inherent elastic properties of the vulcanized caoutchouc colloid, (2) the kind and quality of the rubber used, (3) the state of cure of the compound, (4) aging or after-curing, (5) the specific effects of various organic and inorganic compounding ingredients of reinforcing pigments, (6) the proportion by volume of compounding ingredients incorporated, (7) the effects of vulcanization accelerators.

Aside from the effect of the degree of vulcanization and the inherent qualities of the rubber substance, probably the most important influence on the stress-strain relationship is that of compounding ingredients or "fillers." Physically inert pigments, such as barytes, whiting, fossil flour, pulverized magnesite, coarse clay, lithopone, and many other fillers of rather large particle size, have but little effect on the stress-strain curve. Wiegand[4] showed that there are a few pigments which do have a profound effect on the stress-strain curve, causing a practical disappearance of the curvature in the lower portion when suitable proportions are used. These reinforcing pigments produce greatly increased toughness, hardness (and rigidity), resilient energy, and tensile strength, and are all characterized by a very small particle size.

Each of these pigments has a specific effect upon the properties of rubber. Gas black gives the highest tensile strength, great hardness and rigidity, high resilient energy, but low elongation. Light magnesium carbonate does not produce as great hardness or rigidity as gas black nor quite as high tensile strength, but gives nearly equal resilient energy and greater extensibility. Finely divided clay imparts lower tensile strength, rigidity, hardness, and resilient energy than either gas black or magnesium carbonate. Zinc oxide gives greater extensibility than any of the other pigments, but has much less effect on the hardness and rigidity of the compound.

Although not all the pigments which exhibit a reinforcing effect in rubber have an average particle size below the upper limit usually specified for true colloidal particles (0.1 micron

[12] *J. Soc. Chem. Ind.*, **40** (1921), 268T.

diameter), it must be emphasized that this behavior of finely divided substances in rubber is a genuine colloid phenomenon, since in the strict sense colloid properties involve nothing more than a full development of the surface relations between two substances, one of which is dispersed in the other but not actually in solution.

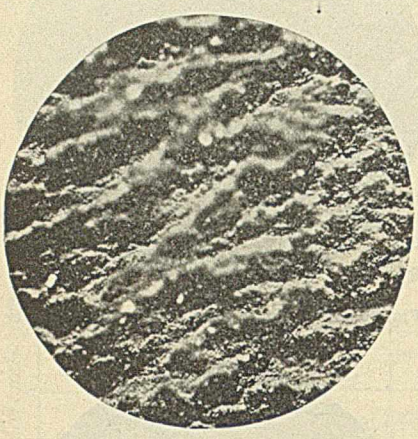

FIG. 17—10 VOLUMES LITHOPONE (50 DIAMETERS)

Wiegand's classification of all rubber pigments into two groups, physically inert fillers and reinforcing pigments, might be profitably extended, it seems, by a further subdivision of reinforcing pigments into those which give great rigidity, high resilient energy and high tensile strength—notably, gas black, lamp black, magnesium carbonate, and *fine* china clay—and those which give less rigidity and resilient energy but high extensibility—including zinc oxide, glue, colloidal barium sulfate, and *coarser* clays. This division cannot, of course, be an exact one, since some pigments—notably, magnesium carbonate—combine the qualities of the two subgroups, giving high resilient energy, rigidity, and tensile strength, and relatively high ultimate elongation.

From the standpoint of the preparation of technical rubber products, assuming the correct (accelerated) cure with respect to tensile strength and aging qualities, it is evident that the modification of the natural stress-strain relations by the use of reinforcing pigments in appropriate amounts is the principal device at our command for determining the position of the stress-strain curve.

COMPOUNDING RUBBER FOR HIGH RESILIENT ENERGY AND ABRASION RESISTANCE

From the discussion of the data above it becomes evident that if a compound is to have the highest possible resistance to abrasion it should have the proper combination of three properties—(1) high tensile strength, (2) high resilient energy capacity, and (3) sufficient hardness (or rigidity). High tensile strength may be obtained by the use of a high-grade accelerated mixing, compounded with correct proportions of suitable reinforcing pigments. The necessary rigidity may also be obtained by the use of reinforcing pigments in sufficient amount. The means by which high resilient energy may be produced in a compound require further consideration.

Let us examine a pure-gum stress-strain curve and determine why the resilient-energy capacity is relatively so small. It is due evidently to the great steepness and curvature of the fore part of the curve, which is so marked that, even though the sample shows high extensibility, the area between the curve and the elongation axis is small. Reinforcing pigments flatten the fore part of the curve and at the same time decrease the ultimate elongation. It will be obvious that for any given tensile strength and any given ultimate elongation, the stress-strain curve which will give the *greatest area* by its projection on the elongation axis (excluding the possibility that the curve might develop an *upward* concavity) is that represented by the diagonal of that particular area between the axes. Such a stress-strain curve might be designated as the "ideal" relationship *from the standpoint of resilient energy capacity.*

Fig. 18 shows a number of such "ideal" stress-strain curves with the corresponding calculated resilient-energy values. The striking fact about these values is that high tensile strength is not accompanied by high resilient energy unless the curve also has high ultimate elongation. This explains why heavily compounded gas-black stocks do not give high resilient energy; they are too rigid, and, although they have high tensile strength, their elongation is low; hence, the area subtended between the curve and the elongation axis is not large.

In order to obtain high resilient energy, therefore, it seems necessary to combine in one compound high tensile strength, relatively high ultimate elongation, and a moderately flat stress-strain curve (rigidity). Since this can be accomplished only to a limited degree by the use of *any one reinforcing pigment alone,* the logical method seems to be to combine the proper pigments in correct proportions, using sufficient proportion of a pigment which gives great rigidity and high tensile strength, together with one or more other pigments which give high extensibility. There is certainly nothing new in the idea of using combinations of fillers in rubber to obtain the desired physical properties, since it has long been common practice in the compounding art to achieve the best qualities for a particular purpose by using a combination of compounding ingredients. To the author's knowledge, however, it has not previously been suggested that the combination of reinforcing pigments does more than give an *average* of the physical properties which might be obtained with the same pigments used separately in the same total proportions. Owing to the peculiar nature of the stress-

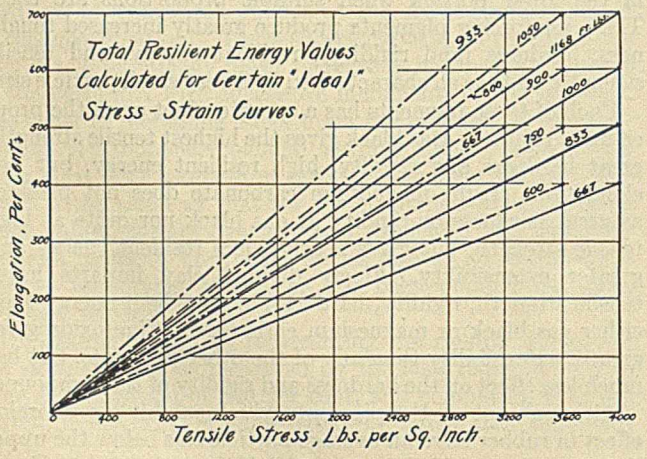

FIG. 18

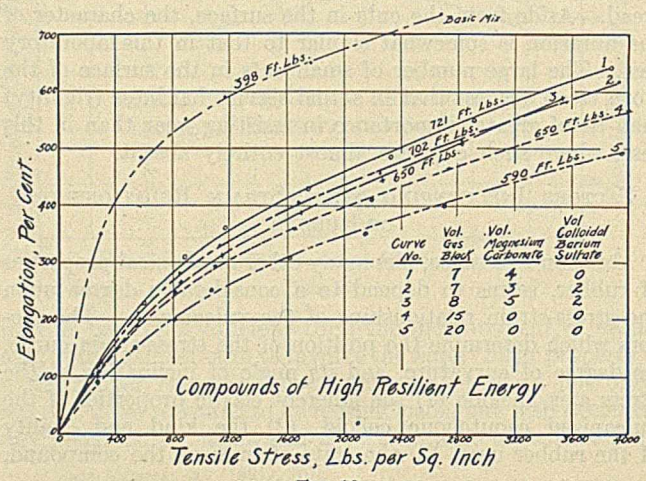

FIG. 19

strain curve for a vulcanized pure gum, it will not be possible to exactly duplicate any of the "ideal" stress-strain curves represented in Fig. 18. It should be possible, however, to prepare compounds in which the stress-strain relationship

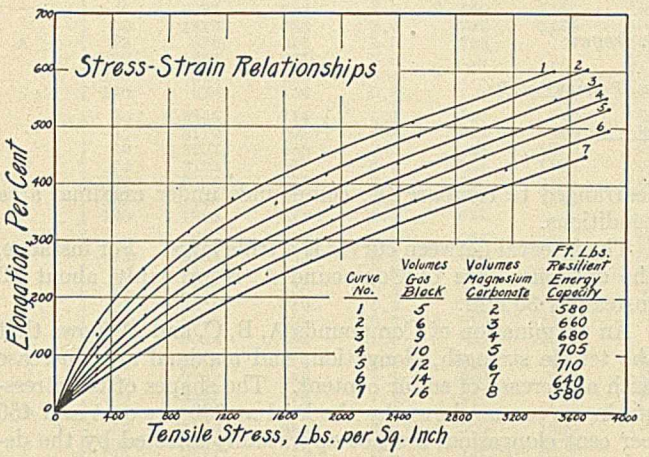

Fig. 20

approaches rather more closely the "ideal" behavior. In Fig. 19 there are shown several stress-strain curves for compounds prepared with this object in view, in a litharge-pale-crepe basic mix. The important point is, no doubt, that a great *increase in resilient energy* can be produced by correct compounding, obtaining at the same time high tensile strength and considerable rigidity.

For the preparation of vulcanized compounds of high abrasion resistance, it is suggested that the following might be tentatively adopted as "compounding principles."

1—The use of a high-grade, accelerated basic mix, cured to give the highest tensile consistent with satisfactory aging qualities.

2—The use in sufficient amounts of combinations of the two types of reinforcing pigments—(*a*) a pigment which gives great rigidity and high tensile and resilient energy, and (*b*) a pigment which gives high extensibility; it should also give some increase in tensile and resilient energy.

3—These pigments to be combined in such proportions that the product of resilient energy and hardness is a maximum.

4—Avoidance of the use of more than very limited proportions of any pigment which does not give an *increase* in tensile strength and resilient-energy capacity. Which combination of pigments can be used to greatest advantage will evidently depend upon the abrasion results obtained and upon such practical considerations as the specific gravity of the compound, volume cost, heat conductivity, hysteresis loss, permanent set, and the ease of compounding and handling.

After considering the abrasion resistance and physical properties of the several pigments, it was anticipated that mixtures of gas black and magnesium carbonate in correct amounts would give especially high abrasion resistance. Both give high abrasion resistance when used alone, both produce high tensile strength, resilient energy, and rigidity, and light magnesium carbonate imparts the high extensibility lacked by stocks compounded with gas black alone. In a previous paper[10] it was shown that a mixture of 6 volumes of gas black and 3 volumes magnesium carbonate gave exceptional resilient energy and tensile strength. Accordingly, a series of compounds was prepared, using the hexa basic mix previously described, and in which the ratio of gas black to magnesium carbonate by volume was 2:1.

Data on Mixtures of Magnesium Carbonate and Gas Black

The stress-strain curves and energy figures for these compounds are shown in Fig. 20. It will be noted that all the compounds have relatively high tensile strength, that several of them have exceptionally high resilient energy (equal to the highest figures obtained with any reinforcing pigment alone), and most of them have relatively flat stress-strain curves and high rigidity.

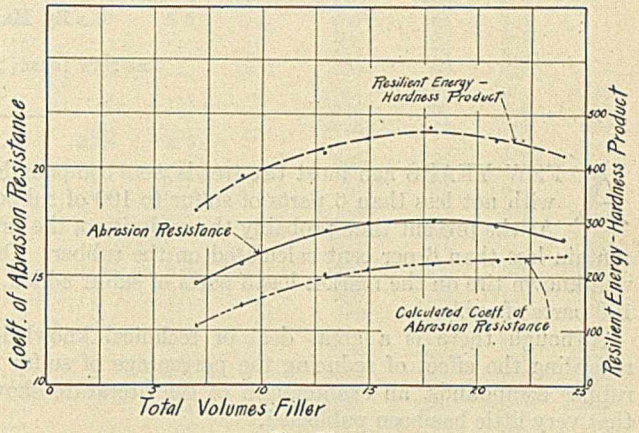

Fig. 21

The high abrasion resistance, which it was anticipated would be given by these compounds containing gas black and magnesium carbonate, is confirmed by the data represented by the curves of Fig. 21. Maximum abrasion resistance is given by compounds containing 10 : 5, 12 : 6, and 14 : 7 volumes gas black to magnesium carbonate. Fig. 22 shows a typical abrasion ring (at 50 diameters) for the 10 : 5 compound. These abrasion-resistance values are nearly as high as those given by gas black alone at its maximum (20 volumes), and the compounds are remarkably strong, rigid, and tough. It will be observed that for all the compounds containing mixtures of these two pigments the measured resistance to abrasion is considerably greater than that calculated from the data for the same proportions of the two pigments used alone. There is evidently, therefore, an additive toughening effect, which seems to lend some support to the previously advanced postulations regarding the modification of the stress-strain relationship by the use of combinations of reinforcing pigments.

In this same graph has been plotted for each of these compounds the value of the resilient-energy hardness product. This curve parallels rather closely the abrasion-resistance curve, and, therefore, for these compounds that product seems to be a reasonably accurate measure of resistance to abrasion. Although this appears to hold true for gas black and magnesium carbonate, it has not yet been established that such a relationship will be found applicable to all reinforcing pigments. It seems improbable, from the data so far obtained, that the product of resilient energy and hardness (rigidity) would be found a satisfactory index of toughness for rubber compounded with inert fillers, oils, rubber substitutes, or plastic substances such as mineral rubber, although this merits further investigation.

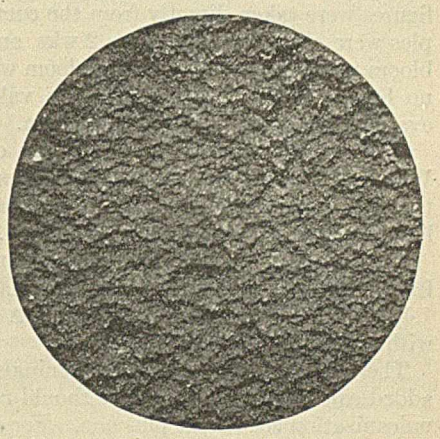

Fig. 22—10 Volumes Gas Black, 5 Volumes Magnesium Carbonate (50 Diameters)

Effect of Variations in the Sulfur and Hexamethylenetetramine Content on Properties of Compounded Rubber[1]

By Harlan A. Depew

THE NEW JERSEY ZINC CO., PALMERTON, PA.

A FEW YEARS ago most tire treads were compounded with not less than 6 parts of sulfur to 100 of rubber. At the present time probably the majority of the tires contain less than 6 per cent calculated on the rubber. One well-known tire on the market has 3 parts of sulfur added to 100 parts of rubber.

Although there is a great deal of technical knowledge regarding the effect of reducing the percentage of sulfur in rubber compounds, an examination of the literature shows that very little has been published.

Recent interest in this subject has led to the presentation of this report from filed data, which were collected in the early summer of 1920, together with recently determined tensile tests on the balance of the original slabs showing the effect of 25 mo. storage.

The compound chosen consisted of 100 volumes of rubber, 10 volumes of XX red zinc oxide, 2 volumes of carbon black to color the compound black, and the curing agents. It was desirable to have a black compound in order to be able to observe the bloom more easily. The sulfur content was varied from 10 to 4 per cent by weight and the accelerator content from $^1/_2$ to 2.2 per cent by weight.

The tensile strength and elongation were determined on an autographic Olsen navy testing machine. The load and area figures were taken directly from the curve sheets. The samples were allowed to stand for 2 wks. and then the degree of bloom was observed. A heavy bloom was chosen as 100 and no bloom as 0. The intermediate values are attempts to evaluate the relative degree of bloom.

Free sulfurs were determined only on the 75-min. cure. Where it is given for other cures it is estimated on the basis that the curve for rubber and sulfur combination is a straight line until most of the sulfur is combined.

The results show that the stocks became nonblooming with free-sulfur contents (calculated to 100 of rubber) of 1.1, 1.4, 1.0, 0.8, 1.2, which average 1.1. A heavy bloom results with 2.0 per cent free sulfur.

Therefore, to produce a nonblooming stock, the total sulfur added calculated on the rubber should not exceed the desired vulcanization coefficient plus one. For example, a nonblooming stock with a vulcanization coefficient of 2.2 should not contain over 3.2 per cent of total sulfur (This does not take into consideration such substances as shoddy, which inhibit blooming to a considerable degree.)

Considering the maximal area under the stress-strain curve to be a criterion of optimum cure, the data have been rearranged to compare the compounds under maximal area conditions.

The interval between curves is a trifle large. For instance, the optimum cure of Compound A, is probably about 40 instead of 30 min.

An examination of Compounds A, B, C, and D shows that the tensile strength, elongation, and maximal area increase with a decrease of sulfur content. The shapes of the stress-strain curves, as shown by the load at 300 per cent and 450 per cent elongation, are not appreciably affected by the decrease in sulfur content.

In a general way there is also an indication that the physical properties are higher with increase of accelerator content. Compound H, with the highest accelerator and lowest sulfur content, has the highest physical properties.

TABLE I—COMPOUNDS INVESTIGATED

	A	B	C	D	E	F	G	H
First latex pale crepe	920	920	920	920	920	920	920	920
Sulfur	92	55	46	37	55	55	46	37
Hexa	15	15	15	15	5	10	20	20
XX red zinc oxide	560	560	560	560	560	560	560	560
Carbon black	34	34	34	34	34	34	34	34
Per cent sulfur on rubber	10	6	5	4	6	6	5	4
Per cent "hexa" on rubber	1.6	1.6	1.6	1.6	0.5	1.1	2.2	2.2

It has been noted by Cranor[2] and others that the vulcanization coefficient at the optimum cure depends considerably upon the accelerator used. The results in Table III indicate that the vulcanization coefficient at the optimum cure is also influenced to a considerable extent by the sulfur content. With 6 per cent of sulfur the vulcanization coefficient is about 2.6 to 2.9, but on reducing the sulfur content to 4 per cent the vulcanization coefficient is 2.0 to 2.2 at the optimum cure.

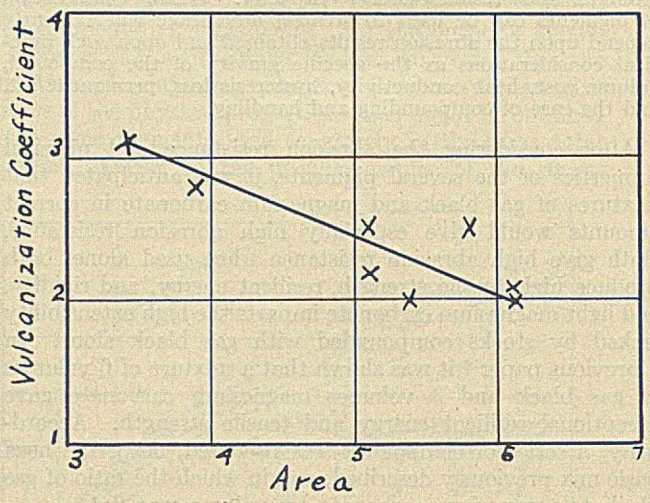

FIG. 1—RELATION BETWEEN THE AREA UNDER THE STRESS-STRAIN CURVE AFTER 25 MONTHS' STORAGE AND THE INITIAL VULCANIZATION COEFFICIENT. COMPARISONS MADE AT THE OPTIMUM CURE

The results of the tests on the samples which had been stored check the statement by Geer[3] and Evans that over-

[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] *India Rubber J.*, **58** (1919), 1201.

[3] *India Rubber World*, **64** (1921), 887.

TABLE II—RESULTS OF THE EXAMINATION OF THE VULCANIZED RUBBER

Sample	Time of Cure at 141° C. Min.	Tensile Strength Lbs./Sq. In.	% Elongation	Area under[a] Stress-Strain Curve	Load—Lbs./Sq. In. 300% Elong.	Load—Lbs./Sq. In. 450% Elong.	Bloom	% Free Sulfur	% Free Sulfur Calcd. to 100 of Rubber	Vulc. Coef.	Estimated Free Sulfur to 100 Rubber	After 25 Months' Storage: Tensile Strength Lbs./Sq. In.	After 25 Months' Storage: % Elongation	After 25 Months' Storage: Area[a]	After 25 Months' Storage: Load—Lbs./Sq. In. 300 % Elong.
A	30	3132	686	6.5	380	940	100	...	...	...	...	2875	625	6.1	520
	45	3037	629	5.9	540	1185	100	...	...	...	...	2530	518	2.3	865
	60	1813	488	3.4	728	1455	100	...	...	...	...	650	165	0.4	...
	75	896	315	1.2	795	...	100	2.82	4.97	5.0	...	700	166	0.5	...
	90	807	261	0.8	...	...	100	...	...	...	...	595	120	0.2	...
	105	546	160	0.4	...	...	100	...	...	...	...	555	78	0.2	...
	120	538	154	0.3	...	...	70	...	...	...	2.0	370	65	0.2	...
B	30	2845	714	6.1	307	760	80	...	...	...	...	2865	665	6.1	420
	45	3110	698	6.1	373	820	80	...	...	...	...	2755	630	5.6	535
	60	3297	665	6.5	484	1070	70	...	...	...	...	2625	575	3.9	665
	75	3103	627	6.0	658	1505	60	1.48	2.55	3.5	...	...	...	...	...
	90	2592	573	5.4	680	1405	10	...	...	...	...	375	125	0.3	...
	105	1618	478	3.4	722	1490	0	...	...	...	1.1	440	116	0.3	...
	120	1288	374	2.2	793	...	0	...	...	...	...	530	125	0.4	...
C	30	2892	733	6.1	255	600	80	...	...	...	...	3120	695	6.2	340
	45	3302	689	6.6	360	945	60	...	...	...	...	3000	625	6.0	415
	60	3483	673	6.8	390	1015	40	...	...	...	...	2945	575	5.8	730
	75	3519	656	6.4	508	1190	20	1.12	1.92	3.1	...	1555	400	2.6	930
	90	3310	619	6.2	603	1350	0	...	...	...	1.4	845	250	1.0	...
	105	2935	598	6.5	650	1350	0	...	...	...	...	720	190	0.6	...
	120	3023	593	5.4	832	1310	0	...	...	...	...	545	135	0.3	...
D	30	2518	717	5.4	262	620	60	...	...	...	...	2615	680	6.2	365
	45	2757	688	5.8	340	855	40	...	...	...	...	2910	655	6.3	525
	60	3387	696	7.3	437	994	30	...	...	...	...	2895	585	5.4	550
	75	3323	665	7.2	513	1100	10	0.87	1.48	2.5	...	1555	425	2.7	805
	90	3270	646	6.6	538	1230	0	...	...	...	1.0	1065	330	1.5	845
	105	2843	617	5.9	553	1475	0	...	...	...	...	630	194	0.6	...
	120	2912	585	5.2	590	1275	0	...	...	...	...	580	165	0.4	...
E	30	1947	690	3.8	216	500	100	...	...	...	...	2200	705	4.1	180
	45	2310	699	5.0	280	865	100	...	...	...	...	2675	675	5.2	290
	60	2735	697	5.6	323	802	100	...	...	...	...	2710	625	5.8	545
	75	2868	677	5.8	356	920	100	1.97	3.38	2.6	...	1800	496	3.3	665
	90	2937	660	6.1	438	1030	100	...	...	...	...	1820	485	3.4	740
	105	2337	620	6.0	493	1110	100	...	...	...	...	593	225	0.5	...
	120	2988	659	6.2	528	1100	100	...	...	...	1.8	465	160	0.4	...
F	30	2200	681	4.0	235	565	100	...	...	...	...	2750	715	6.3	340
	45	2915	702	6.0	344	795	100	...	...	...	...	2990	660	6.3	515
	60	3228	691	7.0	455	980	100	...	...	...	...	2620	590	5.1	655
	75	3200	651	6.5	535	1150	100	1.70	2.92	3.1	...	1500	450	1.2	785
	90	1877	532	3.6	578	1178	80	...	...	...	...	610	195	0.6	...
	105	1488	465	2.7	662	1155	40	...	...	...	...	565	170	0.2	...
	120	1233	413	2.2	725	1425	0	...	...	...	1.0	450	125	0.2	...
G	30	2832	701	6.2	362	820	60	...	...	...	...	2740	695	5.6	325
	45	3257	673	6.9	455	1065	50	...	...	...	...	2675	640	6.1	555
	60	3300	635	6.3	545	1220	30	...	...	...	...	2120	505	3.9	790
	75	3057	613	6.2	625	1350	10	0.88	1.51	3.5	...	820	245	0.8	...
	90	2815	586	5.7	700	1425	0	...	...	...	0.8	745	215	0.7	...
	105	1825	492	3.5	705	1360	0	...	...	...	...	490	120	0.2	...
	120	1822	486	3.5	710	1468	0	...	...	...	...	460	115	0.2	...
H	30	2680	708	5.8	294	705	50	...	...	...	...	2500	710	6.3	390
	45	3182	696	6.3	373	895	40	...	...	...	...	2570	615	5.3	495
	60	3493	678	7.6	468	1100	10	...	...	...	...	2450	555	5.1	715
	75	3232	653	6.9	548	1240	0	0.71	1.21	2.8	1.2	1940	490	3.8	795
	90	3117	618	7.3	585	1240	0	...	...	...	...	1015	325	1.9	845
	105	2757	588	6.5	620	1260	0	...	...	...	...	630	185	0.6	...
	120	2493	569	5.3	623	1385	0	...	...	...	...	545	145	0.4	...

[a] Area is expressed in square inches; 1-in. ordinate = 150 per cent elongation; 1-in. abscissa = 600 lbs./sq. in.

TABLE III—PROPERTIES AT COMPARABLE CURES

Compound	Maximal Area	Time of Cure, Min. 40 Lbs.	Tensile Strength Lbs./Sq. In.	% Elongation	Load—Lbs./Sq. In. 300% Elong.	Load—Lbs./Sq. In. 450% Elong.	Estimated Vulcanization Coef.	% Sulfur on Rubber	% "Hexa" on Rubber	After 25 Mo. Storage: Tensile Strength Lbs./Sq. In.	After 25 Mo. Storage: % Elongation	After 25 Mo. Storage: Area	After 25 Mo. Storage: Load—Lbs./Sq. In. 300% Elong.
A	6.5	30	3132	686	380	940	2.0	10	1.6	2875	625	6.1	520
B	6.5	60	3297	665	484	1070	2.8	6	1.6	2625	575	3.9	665
C	6.8	60	3483	673	390	1015	2.5	5	1.6	2945	575	5.8	730
D	7.3	60	3387	696	437	994	2.0	4	1.6	2895	588	5.4	550
E	6.1(?)	90	2937	660	438	1030	3.1	6	0.5	1820	485	3.4	740
F	7.0	60	3228	691	455	980	2.5	6	1.1	2620	590	5.1	655
G	6.9	45	3257	673	455	1065	2.1	5	2.2	2675	640	6.1	555
H	7.6	60	3493	678	468	1100	2.2	4	2.2	2450	555	5.1	715

cure is the most important factor in the rapid aging of rubber. The tests also show that compounds with low sulfur contents are less affected by overcure than those with higher sulfur contents. It might be more accurate to say that low sulfur compounds overcure less easily. At the optimum cure neither the amount of hexamethylenetetramine nor the amount of sulfur, within the limits of this investigation, greatly affect the aging deterioration. However, there is a rough parallelism between aging, deterioration, and vulcanization coefficients, and it has been noted that low sulfur compounds reach their optimum cure at comparatively low vulcanization coefficients, which would indicate a superiority in aging qualities of low sulfur stocks

The stress-strain curves are stiffened in nearly all cases on aging, as shown by the lead at 300 per cent elongation. The extent of the stiffening is approximately the same for all the compounds.

Fellowship for Study of Soap as a Detergent

The Palmolive Company, of Milwaukee, announces the establishment of a fellowship for the study of the fundamental principles connected with the detergent action of soap.

The fellowship carries an annual stipend of $2000. The fellow will have the privilege of pursuing his studies at any institution in the country which is properly equipped for this purpose. The candidate must possess the equivalent of a master's degree. The fellowship will be awarded by a committee consisting of the following:

W. D. BANCROFT, Professor of Chemistry, Cornell University
E. C. FRANKLIN, President, AMERICAN CHEMICAL SOCIETY
H. N. HOLMES, Chairman, Colloid Division, National Research Council
VICTOR LENHER, Professor of Chemistry, University of Wisconsin
J. C. SELLMER, representing Palmolive Company

Application should be made to Victor Lenher, Chairman, Palmolive Fellowship Committee, P. O. Box 281, Milwaukee, Wis.

Studies on the "Electropure" Process of Treating Milk[1]

By Floyd W. Robison

Robison Laboratories, Inc., Detroit, Mich.

The story of the present so-called "Electropure" process of treating milk is a story of development covering at least a half dozen years. It represents attempts both in this country and in Europe (particularly England)[2] to provide a more certain, more uniform, and more commercial method of milk treatment than that of pasteurization by steam, now quite extensively practiced in the larger cities. It represents the results of diligent search for a "uniformly distributed critical temperature for a minimum period of time," to which milk may be subjected with a maximum of protection against pathogenic microörganisms and with a minimum of destruction to the valuable food properties of the milk.[3]

WITHOUT doubt, pasteurization by steam has accomplished much towards rendering milk of widely varying degrees of purity a usable article of food. That it has made it usable at the expense of valuable food properties[3] is to be regretted but in this as in many other instances, factors of safety and sanitation take first place. Pasteurization by steam is *decidedly* lacking in uniform heat distribution.[4] To overcome this deficiency another error is tolerated—extending the heating period over a maximum time period. In fact, so generally is the lack of uniform heat distribution appreciated that extending the time period is compelled in many localities by statute. In Detroit a city ruling requires that all milk sold at retail except certified and Class A milk shall be pasteurized by holding at a temperature of 142° to 145° F. for 30 min.

Many attempts to develop a method of so-called "flash" pasteurization by steam, by which the milk was flashed to a certain definite temperature, failed because of this very lack of uniformity of heat distribution, and, as a consequence, some of the milk, in fact much of it, escaped treatment entirely. It is this fact that has forced the installation of "holding" in the pasteurization process.

That the prevailing method of pasteurization is destructive in its action upon milk is recognized by the fact that in all ordinances requiring pasteurization, certified milk is expressly exempted. There is most certainly great hazard in the marketing raw of even certified milk—a fact too well appreciated by food scientists to need further proof here. Therefore, it is with much satisfaction that we have observed the high efficiency of this new electrical method of treatment, which, because of the apparent uniformity of the heat distribution, seems to make unnecessary the prolonging of the time of treatment. As a matter of fact, the uniformity of the heat distribution—the uniformly distributed critical temperature for the exceedingly short time necessary—makes it quite apparent that it will now be possible to electrically treat certified and Class A milks, thus insuring these milks against the hazard of contagion and infection without apparently destroying their raw-milk characteristics and properties.

Electropure Process Described

The "Electropure" process consists, in brief, of passing the milk upwards between two carbon electrodes, which are embedded in the opposite walls of a hard-rubber composition material, which in turn is fixed into the interior of a rectangular, upright, metallic box. The milk upon reaching the zone between the electrodes becomes at once the medium of electric conductivity, and as a consequence rises rapidly in temperature until the desired degree is reached, when it automatically flows out through a sensitive thermoregulator to the cooler and to the bottler.

The capacity of the apparatus used in these studies was approximately 500 gal. of "Electropurified" milk per hour. This particular "Electropurifier" was one of a battery of three which was in service in a commercial creamery. The tests reported herein were conducted in a modern creamery in a room set aside for this work, and the milk used for the experiments was taken each morning from the regular raw-milk supply going into Detroit. The tests were conducted daily during the months of July and August, 1921.

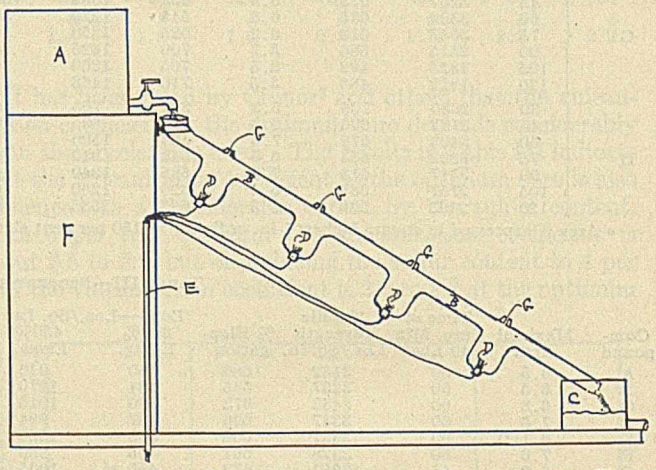

Fig. 1—One of the Early Forms Devised. This Apparatus Never Satisfactorily Passed beyond the Laboratory Stage

Scope of the Studies

The studies herein detailed were undertaken to determine the effect of the "Electropure" process upon pathogenic microörganisms, and particularly *B. tuberculosis*. At the same time opportunity was afforded to determine other factors which have a bearing on the practicability of the process as applicable to a modern creamery. These factors include the effect on reduction of the bacteria ordinarily in milk, the effect on the keeping quality of the milk, the effect on the rising of the cream commonly called cream line, etc.

Ideal Treatment

The ideal process for treatment of milk must cover the following points:

1—Preserve the cream-rising phenomenon, or cream line.
2—Retain the natural milk taste.

[1] Presented before the Division of Agricultural and Food Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

[2] "The Destruction of Bacteria in Milk by Electricity"—Medical Research Committee Special Report No. 49, British Government.

[3] McCollum, "Why Pasteurize the City Milk Supply," *Milk Magazine*, March, 1920; McCollum and Simmonds, "The Nursing Mother as a Factor of Safety in the Nutrition of the Young," *Am. J. Physiol.*, **46** (1918), 275; McCollum and Davis, "The Cause of the Loss of Nutritive Efficiency of Heated Milk," *J. Biol. Chem.*, **23** (1915), 247; Hess, "Newer Aspects of Some Nutritional Disorders," *J. Am. Med. Assoc.*, **76** (1921), 693.

[4] Schorer and Rosenau, *J. Med. Research*, **26** (1912).

TABLE I—EFFECT OF "ELECTROPURE" TREATMENT ON CREAM LINE AND TASTE

No. Expt.	Score of Electropure Treatment[a]					Commercially Pasteurized		
	170° C.	165° C.	163° C.	160° C.	155° C.	(1)	(2)	(3)
Cream Line	%	%	%	%	%	%	%	%
1	75	80	85	95	95	80	100	95
2	85	90	90	95	95	90	95	90
3	85	90	90	92	100	80	75	90
4	80	95	93	95	95	85	85	93
5	95	95	95	95	95	95	95	95
6	90	90	95	95	97	80	80	95
7	85	90	95	95	100	85	95	90
8	90	90	90	92	96	95	90	93
Taste								
1	Slightly cooked	Normal	Normal	Normal	Normal	Slightly cooked	Normal	
2						Slightly ccoked	Slightly cooked	
3						Normal	Slightly cooked	
4						Normal	Normal	Normal
5	Normal	Normal	Normal	Normal	Normal	Normal	Normal	
6						Cooked	Normal	
7						Cooked	Normal	
8						Slightly cooked	Slightly cooked	

[a] Based on raw milk score of 100 per cent.

3—Preserve the activity of the natural vitamins
4—Prolong the keeping quality of the milk
5—Very greatly reduce the total bacteria count
6—Destroy so-called pathogenic microörganisms

Of these No. 3 does not appear here, but is under study and will be reported later.

EFFECT OF "ELECTROPURE" TREATMENT UPON CREAM LINE AND TASTE OF MILK

The cream line should bear a more or less definite relation to the fat content of the milk. This relationship is not at all uniform, for very frequently a milk with a wide cream zone at the top has really less milk fat than one with a narrow cream zone. This is no doubt due in part to the size of the individual fat globules. Prolonged heating tends to decrease the width of the cream zone. Therefore, in any comparative study of the cream zone, it should always be considered in relation to the fat content of the milk.

TABLE II

Milk Used	A pH Score	A Keeping Quality at Room Temp. Hrs.	B pH Score	B Keeping Quality at Room Temp. Hrs.	C pH Score	C Keeping Quality at Room Temp. Hrs.
Raw	50	18	45	12	55	20
Commercially pasteurized	90	25	90	25	90	25
Perfectly pasteurized	100	30	100	25	100	30
"Electropurified" at 170° F.	100	30	100	28	100	32
165° F.	100	30	100	28	100	32
163° F.	100	30	100	28	100	32
160° F.	100	30	100	28	100	32
155° F.	100	30	100	28	100	32

A very noticeable feature of the electro-treated milk is the almost entire absence of any heated or cooked taste in the milk. This has been very apparent in these tests and undoubtedly is of great commercial importance. In the studies of milk pasteurized by steam any noticeable decrease in the cream line was accompanied by a perceptible cooked taste, so that both taste and effect on the cream line combine to discourage efficient pasteurization.

Undoubtedly, one reason for the absence of the cooked taste in electrically treated milk (which is so noticeable in milk pasteurized by steam) is the fact that the electrodes themselves *do not get hot.* They are kept cool by a stream of water, and this seems to prevent the cooked, or scorched, taste, and serves as well to keep the milk from adhering, or sticking, or baking on the electrodes. This feature of water-cooling seems to have a very important bearing on the practicability of the apparatus.

COMPARISON OF THE EFFECT OF ELECTRO-TREATMENT, PERFECT PASTEURIZATION, AND COMMERCIAL PASTEURIZATION UPON THE KEEPING QUALITY OF MILK (pH METHOD–COOLIDGE)

The commercially pasteurized milk reported is the average milk as it comes from the "holder" in pasteurizing plants in Lansing, Mich.

The *perfectly* pasteurized milk reported was prepared by heating a tube of raw milk in a water bath to a temperature of 145° F., maintaining this exact temperature for 30 min., and then immediately cooling in ice water.

The "Electropurified" milk was taken at the effluent of the "Electropure" machine at the various temperatures indicated and immediately cooled in ice water.

EXPERIMENTS TO DETERMINE ABILITY OF "ELECTROPURE" PROCESS TO DESTROY BACTERIUM TUBERCULOSIS WHEN ARTIFICIALLY ADDED TO RAW MILK

The tubercular organs of two guinea pigs, one of which was injected with a human strain and the other with a bovine strain of *B. tuberculosis,* were ground in a sterile mortar with sterile sand. The finely ground tissue and sand were placed in a large bottle of sterile, physiological salt solution. To this mixture was added the growth from six cultures of virulent bovine and human strains of *B. tuberculosis.* The bottle was stoppered, placed in a shaking machine, and shaken for 2 hrs. The bottle was then removed and the suspension of material filtered through sterile absorbent cotton in order to remove large clumps of material and sand. The filtered suspension which contained cells and tubercle bacilli measured 800 cc. by volume.

A direct microscope count of the suspension showed approximately 10,000,000 tubercle bacilli per cc.

PROCEDURE

To each of five 10-gal. cans (approximately 40,000 cc. per can) of raw milk were added 20 cc. of the suspension of tubercle bacilli, and mixed well. The milk was then poured from each of the cans into a large receiving tank and again mixed. Each cubic centimeter of the milk contained approximately 5000 tubercle bacilli.

The experiment was conducted on two succeeding days. The first day, five guinea pigs (weight about 300 g. each) received subcutaneously in the left inguinal region 3 cc. of raw milk (containing approximately 15,000 tubercle bacilli), which had been artificially infected with the virulent culture of tubercle bacilli.

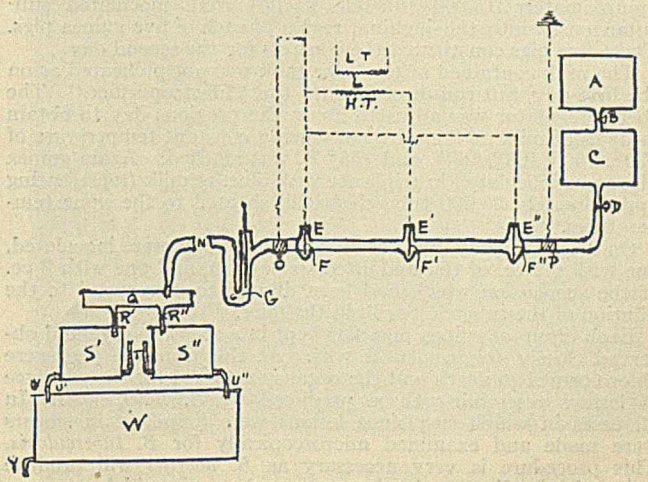

FIG. 2—TYPE OF DEVICE USED BY MEDICAL RESEARCH COMMITTEE OF LONDON IN EXPERIMENTS CONDUCTED BY THAT BODY

TABLE III—EFFECT OF "ELECTROPURE" TREATMENT UPON BACTERIA IN MILK, AS SHOWN BY REDUCTION IN COLONY COUNT—COLONIES PER CC.

Series	1	2	3	4	5	6	7	8	9	10	11	12	Average Reduction %
Raw milk used	4,000,000	4,000,000	1,500,000	2,000,000	10,000,000	12,000,000	6,000,000	12,000,000	10,000,000	2,000,000	1,500,000	2,000,000	
"Electropure" Treatment:													
170° F.	4000	1000	7000	1000	500	16,000	5000	7600	4000	7000	6000	1000	99.9
165° F.	10,000	2000	11,000	2000	2000	11,000	4000	2000	12,000	10,000	2000	2000	99.9
163° F.	12,000	12,000	4000	1000	14,000	3000	5000	2000	14,000	2400	3000	4200	99.9
160° F.	2000	31,000	8000	4000	7400	6000	4000	6000	3000	2000	4000	6000	99.9
155° F.	13,000	10,300	7000	13,000	58,900	21,000	46,000	30,000	103,000	76,000	15,000	12,000	99.4
Perfectly pasteurized	7000	7000	10,000	3000	15,000	18,000	15,000	9000	17,500	5000	6000	12,000	98.0

The milk in the receiving tank was then subjected to steam heat until a temperature of 135° F. was reached. A release cock was then opened permitting the milk to flow into the "Electropurifier." A thermoregulator on the apparatus was adjusted until the stream of milk at the terminal gave a constant-temperature reading of 170° F. A sample at this temperature was collected in a sterile test tube and immediately iced. Following the collection of this sample, the thermoregulator was again adjusted until the stream of milk at the terminal gave a constant

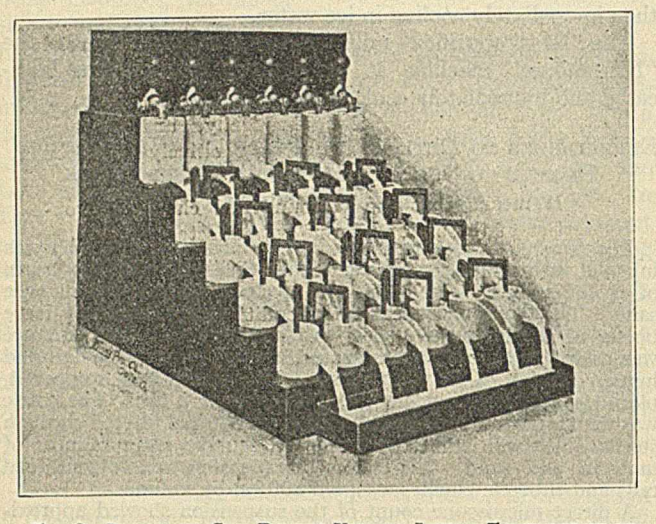

FIG. 3—PORCELAIN CUP DEVICE USED IN INITIAL EXPERIMENTS BY THE AUTHOR IN 1916 AND BY ANDERSON AND FINKELSTEIN AT CAMP MEADE

temperature of 165° F. A sample was collected as above and iced. The procedure described above was carried out in order to obtain samples at temperatures of 163°, 160°, and 155° F.

Following the collection of the samples and icing, three guinea pigs were inoculated intraperitoneally in triplicate with 5 cc. of milk, representing approximately 25,000 tubercle bacilli, obtained at each of the foregoing temperatures.

A similar experiment was conducted on the succeeding day. After the suspension of tubercle bacilli was mixed thoroughly with 50 gal. of raw milk, a large sample of milk was taken from the tank. Three cubic centimeters of this sample (representing approximately 15,000 tubercle bacilli) were inoculated subcutaneously into the inguinal region of each of five guinea pigs. These five pigs constituted the controls for the second day.

The milk contained in the large tank was not preheated as on the first day, but run directly into the "Electropurifier." The thermoregulator was adjusted as on the previous day to obtain samples of milk at the terminal when a constant temperature of 170°, 165°, 163°, 160°, and 155° F. was reached. Again guinea pigs were inoculated in triplicate with 5 cc. of milk (representing approximately 25,000 tubercle bacilli) heated to the same temperatures.

On the second day, two additional control pigs were inoculated, one with 0.2 cc. of the undiluted suspension, and one with 3 cc. of the suspension which had been diluted to correspond to the dilution of the tubercle bacilli in the milk.

Each group of guinea pigs was kept in a separate cage and observed closely for nearly 5 wks. At this time the pigs were chloroformed to death and the organs examined for the presence of lesions resembling those produced by *B. tuberculosis*. In all cases in which suspicious lesions were found, stain smears were made and examined microscopically for *B. tuberculosis*. This procedure is very necessary as *B. abortus* will produce lesions in the liver and spleen of a guinea pig which are very similar to those produced by *B. tuberculosis*.

RESULTS OF INOCULATION OF GUINEA PIGS

SERIES I. CONTROL—*After inoculation with 3 cc. of raw milk containing B. tuberculosis.* Pigs 1 to 10 on autopsy showed one or both inguinal lymph glands enlarged (in some cases with cheesy center), numerous grayish white foci in liver or spleen, and spleen three to four times enlarged. Stain smears from these organs showed *B. tuberculosis* present. Other organs appeared normal.

Pigs 43 and 44 were inoculated with the diluted and undiluted suspensions of tubercle bacilli. On autopsy both pigs showed enlarged mediastinal lymph glands, grayish white foci in liver and spleen. Stain smears from these organs showed tubercle bacilli present.

SERIES II—*After inoculation with 5 cc. of milk used in Series I after preheating and passing through the "Electropurifier" at temperatures from 155° to 170° F.* Pig 14 was found dead on the day following the inoculation, death being due to puncturing of intestine with needle. Pigs 18, 19, and 20 died from some unknown cause; no indication of tubercle lesions. Other pigs of this series showed all organs normal on autopsy.

SERIES III—*After inoculation with 5 cc. of milk used in Series II after passing through the "Electropurifier" at temperatures from 155° to 170° F. without preheating.* Pig 32, inoculated with milk treated at 160° F., on autopsy showed enlarged mediastinal and lymph glands containing a cheesy center, numerous petechial hemorrhages in lungs, numerous foci in liver and spleen, which was four times enlarged. Stain smears from organs showed *B. tuberculosis* present; no lesions at point or region of inoculation. All organs of other pigs appeared normal.

DISCUSSION OF RESULTS

The experiments described in the foregoing paragraphs may be considered a very severe test for the "Electropurifier." It is very improbable that one would ever find as many as 5000 tubercle bacilli in 1 cc. of market milk. In conducting these experiments we have tried to simulate a condition which might exist in milk coming from a herd of cows infected with tuberculosis. In such cases the cellular content of the milk is usually very high, and the tubercle bacilli in large numbers. In this experiment a material in which were suspended numerous body cells and tubercle bacilli was added to the milk.

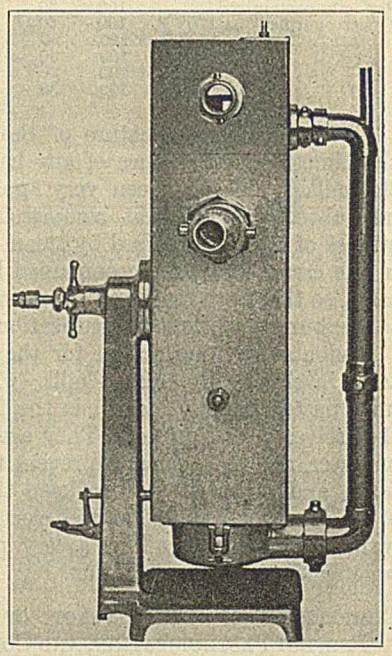

FIG. 4—CUT OF DEVICE USED IN STUDIES REPORTED HEREIN. THIS DEVICE OPERATED DAILY FOR TWO MONTHS UNDER OBSERVATION OF AUTHOR WITH A CAPACITY OF APPROXIMATELY 500 GAL. OF MILK PER HOUR

A study of the results of the inoculated controls (ten in number) reveals that there can be no question of contention as

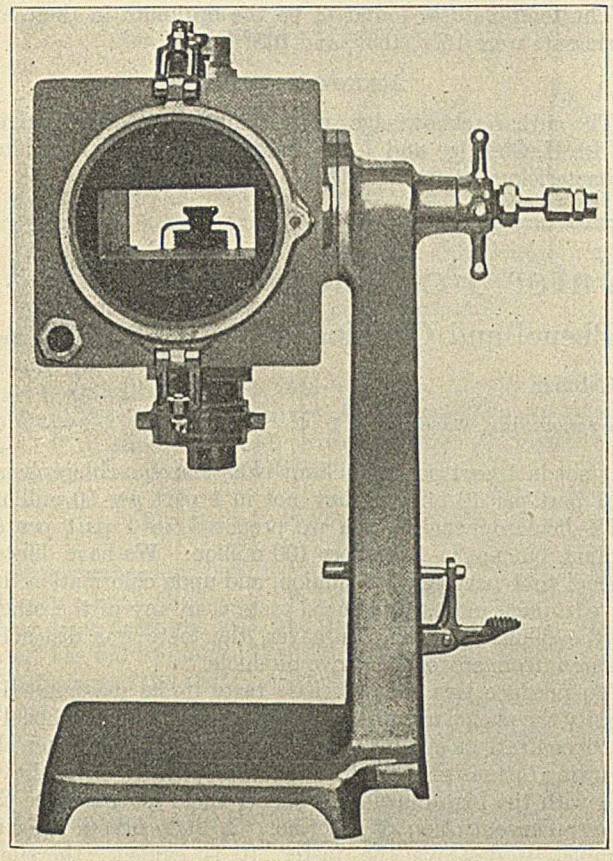

FIG. 5—THE SAME DEVICE AS IN FIG. 4 CLAMPED IN HORIZONTAL POSITION TO SHOW THERMOREGULATOR, THE CHAMBER THROUGH WHICH THE MILK RISES, AND TO ILLUSTRATE THE FACILITY WITH WHICH THE APPARATUS MAY BE CLEANED

to the presence of a sufficient number of tubercle bacilli in the milk to produce active lesions of tuberculosis, as each of the controls showed anatomical changes in several organs characteristic of those produced by *B. tuberculosis*, and a microscopic examination in each case revealed the presence of the organism.

It is important to record that in *all* of the controls there were pronounced tuberculosis lesions at the point or region of the inoculation.

The results of the "Electropure" treatment on the tubercle bacilli in the milk show that only one pig (No. 32 received milk on the second day heated to 160° F.) showed anatomical changes in several organs characteristic of tuberculosis. The presence of tubercle bacilli was established by microscopic examinations of stain smears from the infected organs. It is very probable that this pig may have been infected before inoculation. In fact, there seems no doubt that there was an extensive preinfection in this pig. The lungs were involved and this indicated a different type of infection. Again *there were no lesions* at the point of inoculation as in *all of the controls.*

Also in all of the six pigs inoculated with milk at 155° F. there was no indication of suspicious lesions.

GENERAL REMARKS

The "Electropure" process is a practical process. The apparatus is simple in construction, can be easily and quickly cleaned, and occupies a very small space. When connected with the regenerative cooler, the process becomes quite complete, and lends itself in a decidedly advantageous way to a high standard of sanitary effectiveness.

The facts regarding effects on the cream line and flavor, as well as the keeping qualities of the "Electropurified" milk, are points which will command a decidedly favorable attitude on the part of city milk dealers (creameries) and evoke praise from consumers as well.

The reduction of the bacteria count is phenomenal and no doubt explains to a great degree the remarkable keeping qualities of the "Electropurified" milk.

A point which means much in the operation of the "Electropure" process is the automatic control. This thermoregulator insures that no milk can escape until the treatment has been sufficient to raise the temperature to the desired point. It is this feature that makes it possible to have absolute assurance that all "Electropurified" milk has been effectively processed. The control is automatic and apparently does not depend upon the personal equation.

The application of the electric current is unique in this process. The heat produced is not like that in which the steam system of pasteurization is employed. In the latter the milk is heated by contact with a hot surface and these contact surfaces transmit the heat to the next layer and so on. In this way the surface next to the steam may (and in fact does) get much overheated before the surface further away gets sufficient heat. This may cause a cooked or scorched taste and also a diminution of the cream line.

In the "Electropurified" milk, *the milk itself* is the medium of conductivity and becomes heated through the internal resistance of the milk to the passage of the electric current. The heating is therefore from within, and hence almost instantaneous and very effective. These facts regarding the manner in which the electric current action is effected furnish a very logical explanation of the effects produced as described herein.

ADVANTAGES OF PROCESS

The "Electropure" treatment of milk at temperatures of 155° F. and above completely destroys *B. tuberculosis*. No lower temperatures were used.

The total bacteria content of milk is reduced over 99 per cent by the "Electropure" treatment.

The keeping quality of electro-treated milk is excellent, even better than the most perfectly pasteurized milk and decidedly better than commercially steam-pasteurized milk.

Electro-treated milk has a pleasant, natural taste, and is superior to perfectly steam-pasteurized milk in this respect.

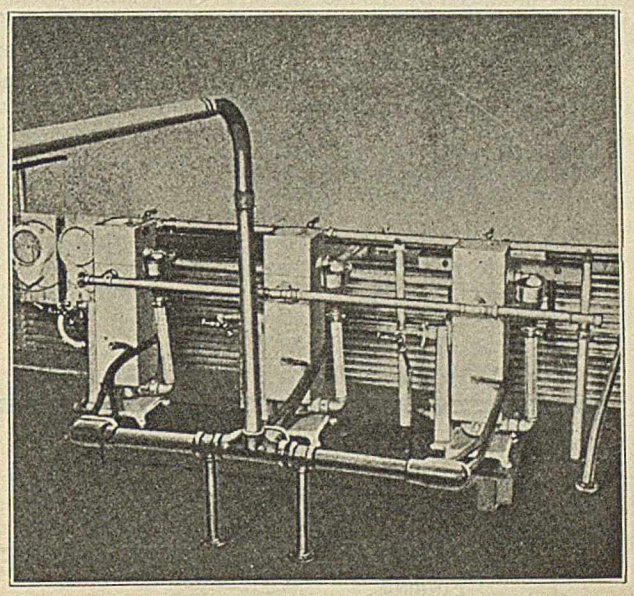

FIG. 6—SHOWING A BATTERY OF THREE "ELECTROPURIFIERS" IN ACTION. THESE HAD A COMBINED CAPACITY OF APPROXIMATELY 1500 GAL. OF MILK PER HOUR. THE REGENERATIVE MILK COOLER IS SHOWN BEYOND THE ELECTROPURIFIERS

The "Electropure" process at 165° F. and below does not adversely affect the cream line as compared with steam-pasteurized milk.

The "Electropure" process is automatic and thus eliminates the personal equation.

The "Electropure" process is practical and "Electropurified" milk merchantable.

The temperatures found to be the optimum in these experiments were 160°, 163°, and 165° F.

ACKNOWLEDGMENT

The author acknowledges with thanks the assistance given by L. H. Coolidge and I. F. Huddleson, research associates in bacteriology at the Michigan Agricultural College.

Phenol-Chlorine Water Pollution[1]

A New Reaction between Phenol and Chlorine

By Edward F. Kohman

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IN 1922 a canner found that a large proportion of his peas were reported by his customers to have a medicinal taste. In many cases this taste was scarcely noticeable in the cold, but was pronounced when the peas were warmed as they would be for serving. Investigation showed this taste to be the result of using water which had been contaminated by the effluent from a coke plant and which was subsequently chlorinated by the city from which the canner secured his water. Upon being informed, the canner used well water when he began canning his pears. He was surprised, therefore, to find that they also had a medicinal taste. An investigation of the factory showed that although well water was used to make the sirup for the pears, city water was still used in the boilers. Just previous to packing the pears in the cans they were covered with warm well water to take the chill off for packing. This well water was warmed by passing live steam through it. Evidently, the substance causing the taste is volatile by steam. The relative location of the coke plant and canning factory are shown in the sketch. Recently, we have learned of another canner who has experienced loss from the same cause and a third who is using city water which has at times an abnormal taste.

This type of water pollution has recently been observed in Cleveland,[2] Milwaukee,[3] Toronto,[4] and other places, and is commonly believed to be due to the formation of chlorophenol. Various dilutions have been made of the chlorophenols normally produced by the interaction of chlorine and phenol. Merck's phenol, *m*- and *p*-monochlorophenol, and Eastman's trichlorophenol could be tasted in 1 part per million of water, but not in 1 part per 10 million; Eastman's *o*-chlorophenol in 1 part per 10 million, but not in 1 part per 50 million; 1,2,4-dichlorophenol, which we prepared, in 1 part per 50 million, but not in 1 part per 100 million. We have diluted phenol to 1 part per 750 million, and upon chlorination this gave a much more pronounced taste than any of the others at the dilution given. Moreover, the taste was distinctly different from any of the above products.

To produce this characteristic taste in its maximum intensity the phenol must be in a high dilution. If the phenol is in concentrations greater than 1 part per 50 million, then the resulting taste is phenolic like the chlorophenols given above; and with the high dilution of phenol there must also be the proper concentration of chlorine. A little excess chlorine completely destroys the taste. It is evident, therefore, that phenol and chlorine under these conditions react differently than they have heretofore been known to react. It would seem that either one of the dichlorophenols other than 1,2,4-dichlorophenol is formed, or there results an entirely new reaction product.

This combination of phenol and chlorine likewise has a very penetrating odor. In approaching the water-works plant of the city on certain days the odor was pronounced 20 or 30 ft. from the door. To a newcomer it was evident in the canning factory on account of the steam-exhaust boxes, although those constantly working in the factory were unaware of it. It is probably for this reason that the superintendent of the factory did not detect the *off*-flavor in his peas and pears.

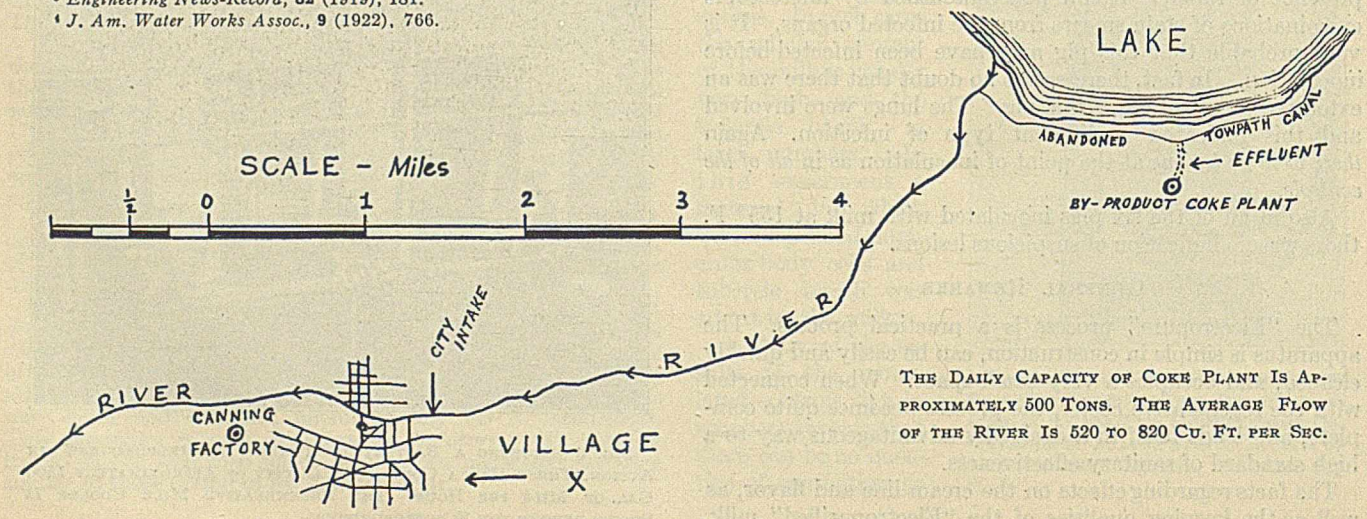
These findings emphasize the necessity that food manufacturers be constantly on guard against water polluted by chemicals or contaminated with algae or other organisms. They can never be sure that some other combination will not prove as disastrous as the one described.

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

[2] *J. Am. Water Works Assoc.*, 9 (1922), 463.

[3] *Engineering News-Record*, 82 (1919), 181.

[4] *J. Am. Water Works Assoc.*, 9 (1922), 766.



THE DAILY CAPACITY OF COKE PLANT IS APPROXIMATELY 500 TONS. THE AVERAGE FLOW OF THE RIVER IS 520 TO 820 CU. FT. PER SEC.

The Decolorizing Action of Bone Black[1]

By Paul M. Horton

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The experimental work of Patterson and Hall on bone black is reviewed. Nitrogenous substances extracted by sulfuric acid are not necessarily the active materials in bone black. Experimental proof is submitted.

THE complex substance known as animal or bone black is the product of the low-temperature distillation of bones. It is of considerable technical importance and therefore has been submitted to much investigation relative to its composition and properties. This paper deals only with its ability to remove color from certain types of solutions.

WORK OF PATTERSON AND HALL

Nitrogen has long been recognized as a constant constituent of active bone char, and the fact that as the activity of a given char decreases with use the nitrogen content is diminished has led to many attempts to prove it to be the active constituent of the char. As early as 1865 Wallace[2] suggested that the active body is a compound of carbon and nitrogen. Patterson,[3] however, was the first to isolate a nitrogenous substance from bone char, which, according to his data, was even more active as a decolorizer than the char from which it was obtained. He stated, therefore, that the active principle of the char was comprised of the nitrogenous bodies present. Hall[4] recently confirmed this conclusion.

Patterson obtained the active substance by treating the purified bone char with about twenty times its weight of concentrated sulfuric acid, followed by filtration through asbestos and dilution of the filtrate with water. A brown to black gelatinous substance soon precipitated from the dilute solution, which was further purified by washing. It was shown by analysis to be a nitrogenous compound similar in composition to the cartilaginous substance of bones. Hall's work consisted in the substitution of alundum for asbestos as the filter.

Zerban[5] has demonstrated that a more active char can be prepared from a mixture of sawdust and casein than can be obtained from the sawdust alone. This seems to support the work of Patterson. However, these chars were all of low power, and there was little conclusive evidence that nitrogenous matter played an important part in the increased decolorizing power. In this instance such an assumption might lead to the conclusion that a char from sawdust mixed with casein could show a certain degree of activity, even though the raw sawdust was known to yield an inactive char. Furthermore, the activity might be expected to follow some simple function of the nitrogen content when the latter is present in small amounts. Neither of these conclusions is substantiated by the data published.

There is no published record of an attempt to correlate the decolorizing power of a char and its nitrogen content. Furthermore, unless the data are confined to bone char—a char unique among chars—no relationship will probably be found. In this laboratory carbon made from C. P. sucrose has been activated many times, simply by selective oxidation. (See also the work of Bartell and Miller.[6]) The analysis of a few typical commercial chars[7] is inserted in further proof of this contention.

NAME OF CHAR	Per cent Nitrogen	Decolorizing Power
Norite	0.136	1.00
Darco	0.265	0.99
Supchar	0.070	1.01
Kelp char	2.000	0.50
Carbrox	0.590	0.95
Bone char	1.060	0.30
Purified bone char	2.570	0.46
C. P. sucrose char	0.000	0.82

Raw rice-bran carbon contains more nitrogen than the most active of the vegetable chars cited above, but it is absolutely inactive. The kelp char and sucrose char used in this series were not activated to the highest degree; therefore, the figures are not as convincing in these cases as they might be.

If it is admitted that the extracted matter from bone black exhibits a certain degree of activity, it is not necessary to postulate that this material represents all, or even a large part, of the active substance of bone black. Certainly, the adsorptive capacity of the extractive would not be expected to exhibit a degree of activity equal to that of the char, since in the latter it is very uniformly distributed over a large surface of inert material, while in the extracted solution it is a more or less gelatinous coagulum. This contention cannot, however, be disproved, owing to the experimental difficulties encountered. For example, if the loss in capacity of the char exactly equaled that of the extract, sufficient proof would have been given that the extract represented the active constituent of the char. Patterson claims to have shown this. Tanner[8] has expressed some doubt of this, however. In view of the theory that decolorization is a specific surface effect, and that the char and the extract are radically different in structure, it is probable that Patterson's work is erroneous in this respect also. Again, direct proof cannot be obtained since the residual char substance remaining after extraction is profoundly modified. It shows considerable solubility in water, the color is grayish instead of black, and it is soft and amorphous. The temperature of extraction, if varied, will not only change the amount but the nature of the extract obtained, as is shown later. Hence, it would be an error in principle to attempt a comparison of the char in the original to the char in the extracted form.

In a series of experiments on the production of an activated carbon by the action of sulfuric acid on sugar or molasses, it was found that the apparent activity of the char decreased upon prolonged washing with water. The char can be washed with water for about 3 hrs. and the runnings will be apparently neutral. However, upon boiling with water the filtrate will become acid again. This throws some light upon Patterson's experiments, for even if his extract were at first neutral, upon standing several hours sufficient acid

[1] Presented before the Division of Sugar Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

[2] *Proc. Glasgow Phil. Soc.*, 6 (1865), 377.

[3] *J. Soc. Chem. Ind.*, **22** (1903), 608.

[4] THIS JOURNAL, **14** (1922), 18.

[5] Louisiana State University, *Bull.* **167**.

[6] *J. Am. Chem. Soc.*, **44** (1922), 1866.

[7] Analyses made by J. L. Farr of the State Experiment Station of Louisiana.

[8] THIS JOURNAL, **14** (1922), 19.

is slowly dissolved from the extract to exhibit considerable bleaching effect upon the caramel test solution. The molasses char mentioned above became absolutely inactive upon boiling with dilute sodium hydroxide, or upon ignition to 400° C. Patterson's dried extract showed no decolorizing effect; hence, it is apparent that occluded acid will account for all the effects observed, as, if the acid is removed by neutralization, volatilization, or reduction (upon ignition the odor of SO_2 is observed from chars made with sulfuric acid), the char becomes absolutely inactive. It should be mentioned in passing that all chars made by the action of sulfuric acid on organic matter are not inactive when neutral.

The change in color of a molasses or caramel solution with change of acidity has been recognized for some time, and is mentioned in publications from this laboratory and by Turrentine and Tanner.[8] This fact, of course, explains the extraordinary activity sometimes exhibited by vegetable chars, as they are often washed with acid to remove soluble ash. The acid is then retained very tenaciously, even when the char is heated to 400° C. However, when the char is tested sufficient acid goes into solution to exert a considerable effect. Patterson and Hall mention the extreme difficulty encountered in washing the acid out of the precipitated matter from the acid extract of bone char. The precipitate tends to pass into a colloidal solution after a certain amount of dilution. It is apparent, therefore, that the treatment given the precipitate removed the acid only superficially. German and Traxler[9] verify the well-known fact—in another connection, however—that it is impossible to wash all absorbed matter from a precipitate when treated on a Büchner funnel. It was found that when three drops of 0.1 *N* sulfuric acid were added to the caramel solution used in testing the extract approximately 25 per cent of the total color was discharged. The extreme importance of this one factor should now be apparent.

Experimental

A large quantity of commercial granulated bone black was first ground to pass through an 80-mesh sieve, suspended in boiling water, and treated with portions of hydrochloric acid until no more gas was evolved. An excess of acid was avoided. The char was then filtered and washed thoroughly, then dried over night at 300° C. The treated char was blacker and more amorphous than the original material.

Twenty grams of the char were then treated with 100 cc. of concentrated sulfuric acid, allowed to stand for 5 hrs. at room temperature, and filtered. The filtration was first made with asbestos, as recommended by Patterson, then the filtrate passed through a dense alundum thimble, as recommended by Hall. The thimble removed a small amount of material from the filtrate through the asbestos, which was shown to be very fine particles of unchanged char. However, on account of the dense and viscous nature of the filter cake, it was found to wash very slowly. Consequently, a small filter of the Pukal type was used in all subsequent work, the cake being sucked dry and then scraped off into a beaker where it was mixed with fresh acid and again filtered. This procedure was repeated until the filtrate became clear. Washing with dilute acid offers no advantages.

After the preliminary work was completed two series of experiments were made. In the first, bone char was extracted with concentrated acid for 1 hr. at the temperature of the water bath. In the second series, the extraction was made with concentrated acid at room temperature for 3 days. The filtration was made through a Pukal filter, the filtrates being treated identically in all cases—i. e., diluted with 5 volumes of water and washed by decantation until the precipitate began to pass into solution. The suspension was then dialyzed for 36 hrs. in running water at about 20° C., then for 6 hrs. in distilled water at 80° C. Collodion sacks were employed as the membrane. In all cases the dialysate was shown to be free from acid by testing with barium chloride. The purified extract thus obtained from the hot acid extraction slowly flocculated upon standing a few hours, while that from the cold extraction remained in suspension for several days. In fact, one specimen was observed for 3 wks., with only a small amount of sedimentation.

The purified extracts were then washed into a liter flask and made to the mark with distilled water. Fifty cubic centimeters of this solution then represented 1 g. of char. One hundred cubic centimeters of each solution were evaporated on the water bath and dried at 110° C. to constant weight. The amount of substance extracted was thus found to average 9.1 per cent for the hot and 7.3 per cent for the cold extraction. The char showed a loss on ignition of 32.6 per cent.

In order to test the extracts, a solution of 10 g. of caramelized sugar per liter was made and buffered according to the method of Turrentine and Tanner.[8] The solution showed no change in color upon adding a few drops of dilute acid of any kind. The solution upon dilution was also shown to follow Beer's law within the limits of the Klett colorimeter used.

Fifty cubic centimeters of the extract and 50 cc. of the caramel solution were mixed and heated on the water bath for 1 hr., and filtered with the use of a little kieselguhr. The comparison was made against the original caramel solution diluted with an equal volume of distilled water, heated, and filtered with kieselguhr.

Results

The extracts showed no decolorizing power whatever, provided the mixtures of bone char and sulfuric acid were carefully filtered. Sulfuric acid seems to cause the char to pass through a filter unless the pores are very fine, in which case the extract will be active.

Conclusion

In conclusion, it is suggested that bone char owes its power of removing color to the presence of active carbon, and that the nitrogenous material serves as a reserve to supply fresh carbon upon reignition. This will explain why the char can be renewed by ignition only as long as it contains nitrogenous material, and why the latter disappears with continued use. This does not preclude the possibility, however, that protein matter may have an important influence upon the form assumed by the carbon upon ignition. In general, it is assumed that the activity of a char from any source is due to the same form of amorphous carbon, produced by the low-temperature decomposition of vegetable or animal substances. Usually, the carbon surface is coated over by a layer of ash or hydrocarbons. The surface may then be exposed, or the char activated, by removal of this film. In the case of sucrose or wood char this may be accomplished by selective oxidation; in the case of highly siliceous material such as rice-hull char the surface may be uncovered by boiling with sodium hydroxide; in the case of bone char the surface film is evidently soluble in water or dilute acids.

This theory will be taken up further in subsequent publications from this department.

[9] *J. Am. Chem. Soc.*, **44** (1922), 463.

Catalytic Oxidation of Anthracene to Anthraquinone[1,2]

By C. E. Senseman and O. A. Nelson

Bureau of Chemistry, Washington, D. C.

The importance of anthraquinone as an intermediate in the manufacture of dyes is shown. Mention is made of the old methods of manufacture, chief among which is the chromic acid method. The catalytic method, patented by Gibbs and Conover, and worked out by the authors, is described in detail.

The apparatus consists essentially of (1) a carbureter, (2) a reaction chamber, and (3) a sublimer for collecting the reaction products. All these parts are made of glass and heated by well-insulated electric heaters. The carbureter is built with two air inlets —one arranged so as to sweep over the molten anthracene and thus carry a definite amount of the hydrocarbon into the reaction chamber, the other arranged so as not to interfere with the work of the first, but to vary the air-anthracene concentration as desired.

Four methods of supporting the catalyst, vanadium pentoxide, are described, thus: (1) by boats, (2) by disks, (3) by pumice, (4) by fusing to a glass tube.

The sublimer, as used during most of the runs, consists of a Kjeldahl flask with neck removed, jointed to the reaction chamber by a ground-glass joint.

Tables accompany, showing the influence of the different variables in the production of anthraquinone. The maximum yield obtained was 81.2 per cent of the theoretical.

The ever-increasing demand for alizarin, indanthrene, and a large number of vat dyes made from anthraquinone makes the methods of producing this intermediate in large quantities, and as cheaply as possible, a problem of much importance. To verify this statement it is necessary only to consider the increase in production and consumption of this compound and of some of the dyes in this class during the last two years.[3]

Historic Sketch

There are a number of methods for making anthraquinone, some of which cannot be considered of much practical value, although from a theoretical point of view they are important. As most of these methods are fully described in the literature, only a brief resumé of the most important ones will be included here.

Anthracene can be oxidized quantitatively to anthraquinone by an excess of chromic acid in glacial acetic acid solution.[4] On a commercial scale this method is too costly, but it may be, and in fact is, used in the quantitative estimation of anthracene. Sulfuric acid may be substituted for glacial acetic, dichromate for chromic acid, and the reaction carried out in aqueous solution, provided the anthracene is in a finely divided state.

This method is probably most extensively used at present. One reason for this is that there should be a ready market in the leather industry for the recovered chromium compound. It has been reported that in Germany, before the war, anthraquinone actually became a by-product in the manufacture of chrome alum for tanning leather. Since anthracene thus served only as a reducing agent, the resultant anthraquinone could be sold at a profit at the same price as the original anthracene.

Other methods have been proposed and in many cases patented. Hofmann, Quoos, and Schneider[5] claim excellent results using sodium nitrate or sodium chlorate in the presence of a large excess of magnesium chloride. Hofmann and Ritter[6] used aqueous sodium hypochlorite containing traces of an osmium salt, and obtained results at ordinary temperatures. Several processes using nitric acid and oxides of nitrogen as oxidizing agents[7] have been suggested and patented. Almost quantitative yields have been claimed for the electrolytic oxidation of anthracene.[8]

In some of these processes the presence of catalysts has been proposed, although not much emphasis has been made of this feature.

Atmospheric oxygen under pressure has been tried for the oxidation of anthracene in aqueous suspension.[9] The catalysts suggested for this process are cupric oxide, or compounds of cobalt, nickel, and lead. Andrews[10] suggests as catalyst the use of oxides or other compounds of molybdenum or vanadium in a solution of sulfuric acid, with an oxidizing agent such as sodium chromate.

The process to which this paper refers, however, is the oxidation of anthracene to anthraquinone, using atmospheric oxygen for the oxidizing agent in the presence of an oxide of vanadium as the catalyst. This process, originated and patented by Gibbs and Conover,[11] formerly of the Color Laboratory, consists essentially in vaporizing the anthracene, mixing the vapors with air, and passing this mixture over oxide of vanadium heated to a high temperature.

Experimental

An attempt has been made to secure data on the following outstanding factors: (1) temperature of reaction chamber, (2) concentration of air-vapor mixture, (3) time of contact between air-vapor mixture and catalyst (this can be only approximate at best), (4) condition of catalyst, (5) support of catalyst. These variables seem to be, to some extent at least, dependent upon each other. For example, the temperature of the reaction chamber may be lowered and the time of contact shortened if the catalyst is in its most active condition. These observations will be brought out more clearly in the tables given on the following pages.

Apparatus—The apparatus designed and used throughout this investigation (Fig. 1) consisted essentially of the following parts:

The reaction chamber, 1, was 16 in. long with an inside diameter of $1^3/_8$ in. It was heated by means of the electric heater, 2, and the temperature was recorded with the pyrometer, 4, inside a glass well. Both ends of the reaction chamber were made with ground-glass joints into which were fitted a carbureter, 3, at one end, and a subliming chamber, 5, at the other. The sublimer was made from a 500-cc. Kjeldahl flask, and in some of the experiments was heated to different temperatures by means of an electric heater. The carbureter was 7 in. long (not including the ground joint connecting it with the reaction chamber) and 1.5 in. in diameter. Two air inlets, 6 and 7, provided the oxygen required for the reaction. By controlling the temperature of

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

[2] Contribution No. 68 from the Color Laboratory, Bureau of Chemistry, Washington, D. C.

[3] U. S. Tariff Commission Census of Dyes and Coal-Tar Chemicals, 1919 and 1920.

[4] Kopp, *Mon. sci.*, [3] 8 (1918), 1159.

[5] *Ber.*, **47** (1914), 1991; D. R. P. 277,733 (1913).

[6] *Ber.*, **47** (1914), 2238.

[7] D. R. P. 283,213 (1913); U. S. Patent 1,119,546; D. R. P. 234,289 (1908).

[8] Brit. Patent 19,178 (1902).

[9] D. R. P. 292,681 (1914).

[10] U. S. Patent 1,324,715.

[11] U. S. Patent 1,417,367. This patent has been assigned by Mr. Gibbs to the Assistant Secretary of Agriculture, who has dedicated the invention to the free use of the people of the United States. This assignment and dedication permit the public to use the invention freely and without payment of royalties, and without obtaining the consent to use this patent from either of the patentees or assignees.

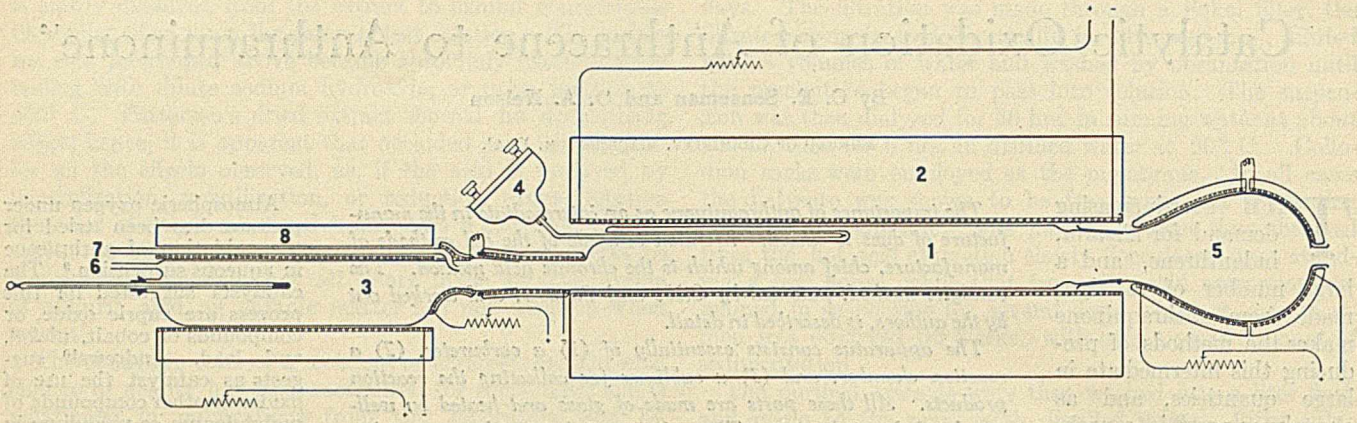

Fig. 1

the carbureter, and thus the rate at which the anthracene would vaporize and the flow of air through both inlets, the concentration of the air-vapor mixture could easily be ascertained. The temperature was measured by a mercury thermometer. All glass parts of the apparatus were made of Pyrex glass.

Procedure—After some pure anthracene had been put into the carbureter the exact weight was obtained. The charged carbureter was then inserted into the electric heater, 8, and connected with the reaction chamber. The empty subliming chamber was tared and joined to the other end of the reaction chamber. After bringing the different parts of the whole apparatus to the required temperatures, air was allowed to flow through both inlets, 6 and 7, at definite rates for definite periods of time, in most cases 1.5 hrs. At the end of each run the air current was shut off. After the carbureter and sublimer were cooled to room temperature, they were again carefully weighed. The loss in weight of the carbureter gave the weight of anthracene used,[12] and the gain in weight of the sublimer gave the weight of the product obtained. This product was then analyzed for anthraquinone according to the volumetric method of analysis developed by the authors.[13]

Discussion of Results

Tables I and II show primarily the effect of varying the temperature of the reaction chamber and also the results obtained by changing the air-anthracene vapor concentration. In Table I the runs made with varying temperature but approximately the same air-vapor concentration are grouped together, while in Table II the runs made with varying concentrations but approximately the same temperature in the reaction chamber and the same rate of flow of air are grouped together. It should be pointed out, however, that these tables show also the effect of supporting the catalyst on different materials, and indirectly the time of contact between the air-vapor mixture and the catalyst. The specific time of contact cannot, of course, be accurately calculated. It is obvious, however, that the larger the catalyst surface over which is passed a specific volume of air-vapor mixture per unit time, the longer the time during which the mixture is in contact with the catalyst. Assuming equal volumes of mixtures passed over the catalyst surface per unit time, the relative time of contact would vary from that where the catalyst is supported on pumice as the longest, to that where the catalyst is supported on plates as the shortest. In all the runs tabulated the catalyst was fused on its support and a considerable number of runs were made in order to get it in its most active condition. The condition of the catalyst will be discussed more fully under a separate heading.

With the catalyst supported by pumice, the best results were obtained when the temperature of the reaction chamber was around 400° C. (Table I). In general, if the temperature of the reaction chamber fell much below the boiling point of anthraquinone, quantities of tarry material were formed in the reaction product and more anthracene escaped unchanged through the reaction chamber. In one of the runs, not tabulated, in which the temperature of the reaction chamber was kept at 350° to 360° C., the reaction product contained a large quantity of unchanged anthracene, some red material, and much charred or tarry matter. The analysis of this product showed only 27.8 per cent of anthraquinone. When the temperature of the chamber was allowed to go much above 400° C., the yield of anthraquinone decreased. While the product as a rule showed a high anthraquinone content, the difference in weight of the anthracene

[12] Since the vapor pressures of anthracene between the melting and boiling points are known [This Journal, 14 (1922), 58], the weight of the anthracene that would be carried over per unit of volume, if saturated, may be readily calculated from Dalton's law of partial pressures.

[13] This Journal, 14 (1922), 956.

Table I—Temperature Effect

Run	Temperature of Carbureter ° C.	Temperature of Reaction Chamber ° C.	Air Flow in Cc. per Min. Through Carbureter	Air Flow in Cc. per Min. Total	$C_{14}H_{10}$ Used G.	G. of $C_{14}H_{10}$ per 1000 Cc. of Air	Wt. of Product G.	$C_{14}H_8O_2$ in Product %	Yield % of Theory	Length of Run Hrs.
1	250 to 255	370 to 375	100	350	11.50	0.274	8.20	89.3	54.5	2
2	240 to 245	385 to 400	100	350	5.80	0.270	4.92	81.6	59.3	1
3	280 to 290	400 to 410	82	364	10.31	0.240	7.68	92.6	59.0	2
4	290	440 to 450	82	364	10.12	0.230	7.41	89.9	56.3	2
5	255 to 260	400 to 410	100	300	4.51	0.250	4.18	84.2	66.8	1
6	255 to 260	420 to 425	100	300	9.50	0.240	8.13	97.5	71.4	2
7	266 to 268	425	100	300	7.96	0.290	7.63	99.0	81.2	1.5
8	262	420	100	300	9.48	0.300	9.44	95.2	81.1	1.75
9	255 to 260	410	100	300	8.70	0.320	8.17	97.9	78.7	1.5
10	250 to 260	450	100	350	15.80	0.274	12.60	91.4	62.4	2.75
11	265	410 to 415	125	300	8.77	0.486	7.75	74.9	56.7	1
12	255 to 260	435 to 450	100	300	8.8	0.486	6.92	94.0	63.3	1
13	255 to 257	390	100	300	7.25	0.266	6.24	91.6	67.5	1.5
14	255 to 257	400	100	300	6.33	0.233	5.15	98.1	68.3	1.5
15	265	435 to 450	70	270	4.65	0.285	3.31	98.8	60.2	1
16	255 to 260	390 to 400	100	300	8.18	0.303	7.14	86.5	64.6	1.5
17	263 to 265	410 to 415	100	300	8.29	0.306	6.75	98.2	68.4	1.5
18	265	425	100	300	8.48	0.313	7.05	94.8	67.5	1.5

Note: In all runs in Tables I and II a fused catalyst is used. In Runs 1 to 4 the catalyst support is pumice; in Runs 5 to 12, a glass tube; and in Runs 13 to 18, perforated disks.

TABLE II—ANTHRACENE-CONCENTRATION EFFECT

Run	Temperature of Carbureter ° C.	Temperature of Reaction Chamber ° C.	Air Flow in Cc. per Min. Through Carbureter	Air Flow in Cc. per Min. Total	$C_{14}H_{10}$ Used G.	G. of $C_{14}H_{10}$ per 1000 Cc. of Air	Wt. of Product G.	$C_{14}H_8O_2$ in Product %	Yield % of Theory	Length of Run Hrs.
19	280 to 285	375 to 380	82	364	9.18	0.210	7.03	90.4	59.3	2
1	250 to 255	370 to 375	100	350	11.50	0.274	8.20	89.3	54.5	2
20	250 to 255	400	100	350	5.90	0.143	3.35	69.3	33.7	2
21	250 to 255	400 to 410	100	350	12.50	0.200	8.10	88.8	49.3	3
22	250 to 255	400	100	350	7.30	0.231	5.10	90.6	54.2	1.5
23	240 to 245	385 to 400	100	350	5.80	0.274	4.92	81.6	59.3	1
24	240 to 245	385 to 400	100	350	7.93	0.374	6.55	71.4	50.5	1
25	275 to 280	400 to 410	85	415	9.46	0.190	5.49	89.8	44.6	2
26	275 to 280	400 to 410	85	415	12.62	0.253	9.09	90.0	55.5	2
27	280 to 285	400 to 410	100	415	19.15	0.386	11.71	86.1	45.1	2
28	280 to 285	400	85	415	20.75	0.417	17.56	55.0	39.8	2
29	250	450	80	380	4.65	0.137	1.80	Very poor	Not analyzed	1.5
30	260 to 265	450 to 460	120	420	8.90	0.220	5.30	90.1	45.9	1.75
31	285 to 290	440 to 450	85	415	14.22	0.285	11.14	82.1	55.1	2
32	265 to 267	410 to 420	100	300	3.98	0.220	2.81	73.1	44.2	1
5	255 to 260	400 to 410	100	300	4.51	0.250	4.18	84.2	66.8	1
9	255 to 260	410	100	300	8.70	0.323	8.17	97.9	78.7	1.5
11	265	410 to 415	125	300	8.77	0.486	7.75	74.9	56.7	1
10	250 to 260	450	100	350	15.80	0.274	12.60	91.4	62.4	2.75
33	260 to 265	450	120	320	18.80	0.390	16.90	67.6	52.0	2.5
14	255 to 257	400	100	300	6.33	0.233	5.15	98.1	68.3	1.5
13	255 to 257	390	100	300	7.25	0.266	6.24	91.6	67.5	1.5
34	265 to 267	410 to 415	100	300	8.55	0.316	7.50	85.4	64.1	1.5
35	265 to 267	410 to 415	100	300	10.45	0.386	9.00	77.7	57.3	1.5

NOTE: In Table II Runs 19 to 31, inclusive, catalyst support is pumice; in Runs 32, 5, 9, 11, 10, and 33 the support is a glass tube; in Runs 14, 13, 34, and 35 disks support the catalyst.

used and the product obtained was invariably greater, thus lowering the yield. This would indicate that at the higher temperatures the oxidation proceeded beyond the anthraquinone stage, possibly even to carbon dioxide and water.

Runs 5 to 12, inclusive, show the results obtained with the catalyst supported on a glass tube. The catalyst was fused on a glass tube about 8 or 10 in. long, with an outside diameter of $^3/_4$ in. The ends were sealed, except for an opening for the pyrometer. This tube, when inserted into the reaction chamber, left a space of about $^5/_{16}$ in. between the catalyst and the inner wall of the reaction chamber. The reaction mixture thus had to come in close contact with the catalyst while passing through the entire length of the inserted tube.

The best results were again obtained when the temperature of the reaction chamber was held at 400° to 425° C. Permitting the temperature to rise much above this point caused a decrease in the yield (Run 10), while at lower temperatures similar results were obtained.

The last six runs tabulated in Table I give the results obtained when the catalyst was supported on perforated disks. The results indicate once again that the highest yields were obtained at a temperature around 400° to 425° C. Run 15 indicates that some of the anthracene had been completely destroyed, since the yield was low, but the reaction product proved to be almost pure anthraquinone.

Table II was prepared to show primarily the effect of varying the concentration of the anthracene vapors in the reaction mixture. The concentration is tabulated in Column 7, calculated to the weight of anthracene carried over per 1000 cc. of air.

The highest yields of anthraquinone were obtained in each individual group when the concentration of anthracene was between approximately 0.220 and 0.320 g. of anthracene per 1000 cc. of air (Runs 19 and 1, 22 and 23, 26, 30 and 31, 5 and 9, 10, 14, 13 and 34). In all other runs the yields of anthraquinone decreased when the anthracene concentration fell below or rose above these limits.

The time of contact between the reaction mixture and the catalyst has a marked effect on the yield of anthraquinone. Consider Runs 22 and 25, and 23 and 26. Runs 22 and 25 have approximately the same air-vapor concentration but the time of contact is longer in Run 22, resulting in a correspondingly higher yield of anthraquinone. The same is true of Runs 23 and 26.

These observations permit some conclusions as to the conditions under which the process must be run in order to get the optimum yield of anthraquinone. Table III shows the best results obtained in approximately 150 runs.

TABLE III

Run	Temperature of Reaction Chamber ° C.	Total Air Flow Cc./Min.	G. of $C_{14}H_{10}$ per 1000 Cc. Air	Support for Catalyst	$C_{14}H_8O_2$ in Product %	Yield % of Theory
2	385 to 400	350	0.27	Pumice	81.6	59.3
3	400 to 410	364	0.24	Pumice	92.6	59.0
7	425	300	0.29	Glass tube	99.0	81.2
8	420	300	0.30	Glass tube	95.2	81.1
9	410	300	0.32	Glass tube	97.9	78.7
13	390	300	0.266	Disks	91.6	67.5
16	390 to 400	300	0.303	Disks	86.5	64.6
17	410 to 415	300	0.306	Disks	98.2	68.4
18	425	300	0.313	Disks	94.8	67.5

With the catalyst supported on a glass tube, the temperature of the reaction chamber held between 410° and 425° C., the rate of air flow 300 cc. per min., and the weight of anthracene carried over approximately 0.3 g. per 1000 cc. of air, higher yields of anthraquinone were obtained than under any other conditions. There was, however, one drawback in supporting the catalyst in this manner. This will next be discussed more fully.

SUPPORT OF CATALYST

Three substances were used to support the catalyst—pumice, a glass tube, and perforated plates made from pressed asbestos. The catalyst was prepared and applied as follows:

A thin paste of vanadium pentoxide and pure water was prepared, and, in the case of pumice, the pieces of this material were dipped into this paste and allowed to take up as much of the catalyst as they could. They were then heated in a blast lamp until the vanadium pentoxide had melted. The catalyst was prepared and applied in a similar manner to the perforated asbestos plate but was applied with a brush to the glass tube and then fused.

Although the best yields were not obtained with the catalyst supported on pumice, this material was very desirable for this purpose, because of the ease with which it took up the catalyst and the way it held it. Since the yields obtained when the catalyst was supported in this way and on asbestos plates were invariably lower than those obtained when it was supported on glass, these materials would seem to have a retarding effect. If, however, the unattacked anthracene were recovered, as it very readily could be, this retarding effect would not be of much importance. The best yields were obtained with the catalyst supported on glass, but it was very difficult to make the fused vanadium

pentoxide stick on this material for any length of time. After eight or ten runs most of the catalyst had peeled, necessitating preparation and application of fresh material. A few runs were also made with vanadium pentoxide powder in porcelain boats, or perforated disks made from fused vanadium pentoxide, but with results so discouraging that these methods of supporting the catalyst were abandoned as being of little value.

Condition of Catalyst

The condition of the catalyst had a very marked effect on the yield of anthraquinone and on the general quality of the different products of oxidation. With the fresh, brown vanadium pentoxide the yield of anthraquinone was very low, and some unchanged anthracene and large quantities of a reddish brown product were invariably produced. While these red compounds were not analyzed, from their appearance and other physical properties it is believed they were lower oxidation products of anthracene. This clearly indicated that with the catalyst in this condition, the transformation of anthracene into anthraquinone left much to be desired. These results were obtained even though the temperature of the reaction chamber was kept around 500° C. However, after a number of runs had been made, during which the color of the catalyst changed from brown to a shade that seemed to be a mixture of brown and bluish green with the darker colors predominating, better yields of anthraquinone and smaller amounts of the red material were obtained at much lower temperatures.

The pentoxide alone does not seem to make as active a catalyst as when it is mixed with one or more of the lower oxides. While the area of the surface exposed or the fineness of the division of the catalyst may affect the activity, the observations thus far at hand are not very consistent in this respect. For example, better results were obtained after the catalyst had been fused to the side of the reaction chamber or the pumice, thus decreasing the surface area, than were obtained before fusion, while the catalyst was in the form of a powder. However, in other cases poor results were obtained in the first few runs after the catalyst had been fused to the support, but increased yields resulted after portions of the catalyst began to peel, when the surface was much larger.

Whenever fresh catalyst was introduced its activity increased, and the yield of anthraquinone became better up to a certain limit as the runs were continued. In other words, continued usage of the catalyst improved it, until a condition was reached when, by keeping the different variables the same, constant and reproducible yields would result.

From the observations recorded some idea might be formed of the mechanism of the reaction. As already indicated, the most active catalyst for this reaction is a mixture of vanadium pentoxide and lower oxides of vanadium. Since the original material was always the pentoxide, some of this must have been reduced by the anthracene vapors. This was further verified by placing a small quantity of anthracene and vanadium pentoxide in a glass tube, evacuating it to about 2 mm., sealing it, and then heating it to about 400° to 500° C. for 1 hr. The color of the vanadium oxide changed from brown to bluish green. Upon breaking the tube and analyzing the product, it was found that about 12 to 15 per cent of the anthracene had been oxidized to anthraquinone. Also, the bluish green compound could readily be reoxidized to the brown in a current of air at 400° to 500° C. These results seem to indicate that the oxygen for the reaction is given up by the vanadium pentoxide, and that the air then reoxidizes the resultant lower oxides back to the pentoxide, rather than that the air oxidizes the anthracene to anthraquinone directly. Equations representing these reactions would be somewhat as follows:

$$V_2O_5 + C_{14}H_{10} = \text{Lower oxides of vanadium} + C_{14}H_8O_2 + H_2O$$
$$\text{Lower oxides of vanadium} + O_2 = V_2O_5$$

It has been mentioned that no comparable results for the surface exposed or fineness of division of the catalyst were obtained. This, it seems, is to be expected if the mechanism of reaction is one of alternate reduction and oxidation, for here the speed of the reaction would depend more upon the ease with which, or the rate at which, the catalyst would reduce and oxidize, than upon the area of the surface.

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Since this paper was written an article on "Catalytic Formation of Water Vapor," by Pease and Taylor,[14] in which results somewhat analogous to the ones observed in our work are enumerated, has appeared. These investigators state that at the temperature at which the catalyst (copper) is readily both oxidized and reduced (200° C.) "the mechanism must be, in part at least, one of alternate oxidation and reduction." They also point out that the copper oxide formed during a catalytic experiment makes a more active catalyst than does the original material. The results obtained in our work seem to indicate that the same statements may be made regarding vanadium oxide.

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A New Modification of Dühring's Relation[1]

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THE PRACTICAL value of Dühring's relation between temperature and vapor pressure has been brought out by Dodge.[2] He plots the temperature of one liquid at various vapor pressures against the temperature of another liquid at corresponding vapor pressures. The line drawn through the points is nearly a straight line. Evidently, two points will determine the curve. Lewis and Weber[3] have added to the usefulness of the relation by indicating how the slope of this line can be found by calculation, thus making only one point necessary to draw the line.

The author has modified Dühring's relation so that it is now a relation between temperature and mol vapor concentration. In this form it may conform more closely to actual conditions, and is more simple to handle. This change from vapor pressure to mol vapor concentration avoids the difficulties experienced by Ramsay and Young,[4] who have also modified this relation.

Dühring's equation is:[5]

$$T'_A - T_A = K\,(T'_B - T_B)$$

where T'_A = any temperature of the substance in question
T'_B = temperature at which a reference substance has the same vapor pressure as the substance in question has at T'_A
T_A and T_B = any other temperatures at which the two substances have the same vapor pressure

If this relation holds true, then plotting the temperature of substance A against the temperature of substance B will give a straight line. Two points, as pointed out by Dodge, will determine the line. Lewis uses only one point, determined by experiment. He determines the slope $\frac{\Delta T_A}{\Delta T_B}$ by the following formula:

$$\frac{\Delta T_B}{\Delta T_A} = \left(\frac{L_A}{L_B}\,\frac{T_B}{T_A}\right)^2$$

where L = latent heat of evaporation of the respective substance. He obtains this equation by dividing the Clausius equations for the two substances, thus eliminating the pressure term.

Hildebrand[6] has found that the entropy of evaporation $\left(\frac{L}{T}\right)$ is constant for normal or nonpolar liquids, if the temperature represents the absolute temperature where the mol vapor concentrations are the same, in place of the vapor pressures (boiling points). Using the same idea as applied to the Dühring relation, the following relation between temperature and mol vapor concentration exists. The value K, which represents the slope of a new straight line, can be found by substituting Hildebrand's relation $\frac{L}{T} = K_H$ and solving for K.

$$\frac{L'_A}{K_1} - \frac{L_A}{K_2} = K\left(\frac{L'_B}{K_1} - \frac{L_B}{K_2}\right)$$

$$K = \frac{\dfrac{L'_A}{K_1} - \dfrac{L_A}{K_2}}{\dfrac{L'_B}{K_1} - \dfrac{L_B}{K_2}}$$

If the temperature differences taken are small the value L will not change enough to affect the accuracy of the results; therefore we call the two values of L the same.

$$K = \frac{K_2L_A - K_1L_A}{K_2L_B - K_1L_B} = \frac{L_A}{L_B}$$

[1] Received October 14, 1922.
[2] This Journal, **14** (1922), 569.
[3] *Ibid.*, **14** (1922), 486.
[4] *Phil. Mag.*, [5] **20** (1885), 515; **21** (1885), 33; **22** (1886), 37.
[5] Temperatures used throughout article are absolute.
[6] *J. Am. Chem. Soc.*, **37** (1915), 970.

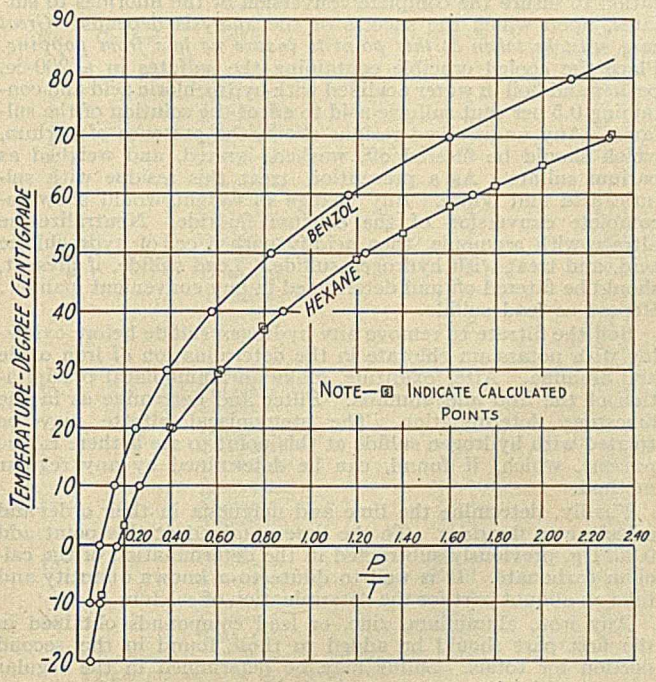

Fig. 1

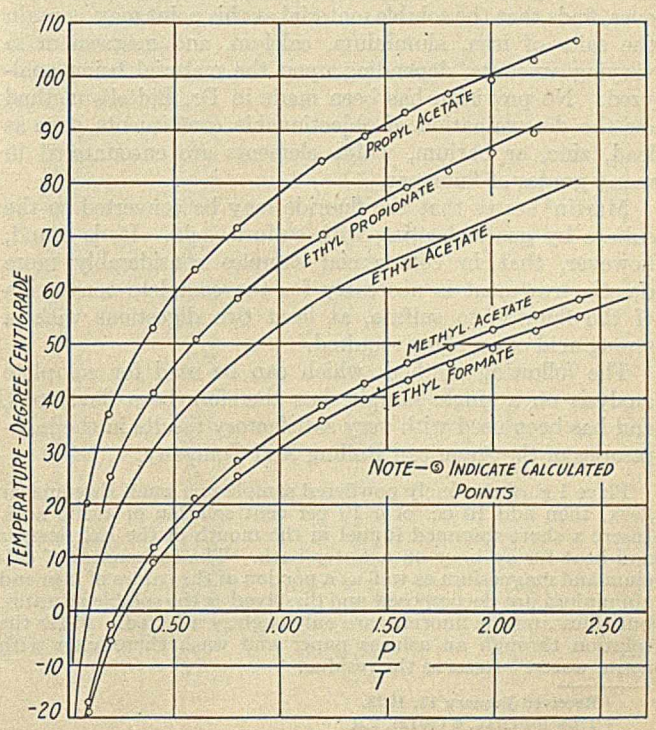

Fig. 2

Substituting the Hildebrand equation once more, we can obtain the value of K in terms of temperature.

$$K = \frac{T_A}{T_B} \text{ or } \frac{T'_A}{T'_B}$$

The Dühring modified relation now becomes

$$T'_A - T_A = \frac{T'_A}{T'_B}\left(T'_B - T_B\right)$$

where T'_A = any temperature of the substance in question

T'_B = temperature at which a reference substance has the same mol vapor concentration as the substance in question has at T'_A

T_A and T_B = any other temperatures at which the two substances have the same mol vapor concentration

This means that if one knows the temperature–mol vapor concentration curve for one liquid and one point on a similar curve for another liquid, the entire curve for the latter can be calculated. It is reasonable to believe, however, that the accuracy of the results can be improved if the reference liquid is the same type of compound as the liquid the curve of which is to be determined. If vapor pressure is desired rather than mol vapor concentration, the gas laws may be assumed to hold and the pressure calculated, especially if the vapor pressures are below atmospheric.

To test out the practical value of this modified relation, a few curves have been drawn from data given by Landolt and Börnstein, and various points calculated. The data used were vapor pressures and a value P/T was calculated (assuming the gas laws held) to represent the mol vapor concentration. In Fig. 1 the benzol curve was taken as the reference, and the points along the hexane curve were calculated. In Fig. 2 the curve for ethyl acetate was taken as the reference and the points on the propyl acetate, ethyl propionate, methyl acetate, and ethyl formate curves were calculated. Realizing that the data used were not real mol vapor concentrations and considering the probable accuracy of experimental work, the deviations are extremely small.

Analysis of Fluorspar[1]

By C. E. Gifford

The American Rolling Mill Co., Middletown, Ohio

THERE is often occasion for the complete analysis of fluorspar (calcium fluoride), especially when the material is bought upon a specification basis, or if the presence of any undesirable impurities, such as lead, zinc, or barium, is suspected.

The published methods are found to be not only unsatisfactory and incomplete, but misleading in many of the statements given. For instance, Dr. Bidtel's method,[2] as published in Scott's "Methods of Chemical Analysis," states that the loss in weight found upon burning the residue insoluble in 10 per cent acetic acid less 0.0015 g. (the amount of calcium fluoride soluble in acetic acid under the condition named) is to be reported as calcium carbonate. The author, however, finds that the soluble material at this point may contain the salts of iron, aluminium, calcium, and magnesium in varying amounts, depending upon the material being analyzed. No provision has been made in Dr. Bidtel's method for the determination of objectionable constituents, such as lead, zinc, or barium, which elements are encountered in many grades of fluorspar.

Martin[3] states that the fluoride may be converted to the sulfate by gentle heating with sulfuric acid. It is found, however, that in commercial samples considerably more drastic treatment is necessary for the complete conversion of the fluoride to sulfate, at least two digestions with a strong acid often being required.

The following method, which can be used for complete analysis on a single sample, has therefore been developed, and has been used with very satisfactory results in the laboratories of the American Rolling Mill Company:

Place 1 g. of the finely powdered sample in a small Erlenmeyer flask, then add 10 cc. of a 10 per cent solution of acetic acid. Insert a short-stemmed funnel in the mouth of the Erlenmeyer and heat for an hour on a water bath. The carbonates of calcium and magnesium as well as a portion of the oxides of iron and aluminium are decomposed and dissolved as the soluble acetates, but silica and the fluorides are only slightly affected. Filter the solution through an ashless paper and wash thoroughly with warm water. Reserve the residue.

Acidify the acetic acid extract with sulfuric acid and evaporate in order to convert the calcium fluoride to calcium sulfate. Dissolve in a small amount of hydrochloric acid and determine the oxides of iron and aluminium, lime, and magnesia in the solution. From the lime obtained subtract 0.0011 g. CaO, the equivalent of the calcium fluoride soluble under the above treatment. Calculate the lime and magnesia and report as the carbonates. Should the presence of lead be suspected, it may be separated by hydrogen sulfide previous to the precipitation of iron and alumina.

Ignite the residue obtained in the treatment with acetic acid, and weigh. Add hydrofluoric acid to the residue in the crucible and evaporate very carefully to dryness, best on a hot plate. Repeat the addition of hydrofluoric acid, and again evaporate to dryness. Heat to dull redness, cool, and reweigh. Report the loss in weight as silica.

To the residue add 5 cc. of sulfuric acid and heat to redness after evaporation of the acid. Repeat this addition and evaporation to insure the complete conversion of the fluorides to sulfates, upon which the success of the analysis depends. *Great care must be taken at this point to insure no loss from popping.* Place the cooled crucible containing the sulfates in a 200-cc. beaker and boil in water acidified with hydrochloric acid and containing 0.5 per cent sulfuric acid to effect the solution of the sulfates. Any undissolved residue shows the presence of barium, which should be filtered off, washed, ignited, and weighed as barium sulfate. As a precaution, treat this residue with sulfuric acid and ignite. Any change in weight would show incomplete conversion of the calcium fluoride. Neutralize the filtrate with ammonia, then acidify with 5 cc. of hydrochloric acid, and treat with hydrogen sulfide. Lead sulfide, if present, should be filtered off and determined in any convenient manner. Report as lead sulfide.

Boil the filtrate to remove any hydrogen sulfide before oxidizing with potassium chlorate in the determination of iron oxide and alumina. After oxidizing, make an ammoniacal precipitation of the iron and alumina. Filter and determine as in the limestone determination. The ammoniacal filtrate may be treated with hydrogen sulfide at this point to see if there is zinc present, which, if found, can be determined by any regular method.

Finally, determine the lime and magnesia in their order and calculate to fluorides. To the lime obtained at this point add 0.0011 g. previously subtracted in the determination of the calcium carbonate. It is well to dilute to a known quantity and take an aliquot part for the determination of calcium.

Any iron, aluminium, zinc, or lead compounds obtained in the first part should be added to those found in the second portion for totals. Sulfur may be determined in the regular manner with precautions as given in Martin's method.[3]

[1] Received January 11, 1923.

[2] This Journal, 4 (1912), 201

[3] *Ibid.*, 1 (1909), 462.

Oxygen and Perforations in Canned Fruits[1]

By Edward F. Kohman

Research Laboratory, National Canners Association, Washington, D. C.

IT WAS RECENTLY[2] pointed out that it is important to exclude oxygen from the can to protect vitamin C in canned foods. This has long been considered an important precaution to minimize the tendency of certain fruits to perforate because of the well-known corrosive action of oxygen on tin plate. In fact, the longer exhausts and higher closing temperatures that are in vogue at present are the result of attempts to eliminate oxygen as far as possible.

There are no data available, however, which indicate the relative effect of varying amounts of oxygen in the can. It has been suggested that oxygen may have a catalytic effect, and for this reason small amounts might be relatively more harmful than larger amounts. This question is of practical importance because if its effect follows the law of mass action, then the benefits derived from excluding it as far as possible would be commensurate with the pains taken. If, on the other hand, small amounts act catalytically, the problem of its exclusion would be a less promising one.

It is common belief that any oxygen left in the can at the time of closure disappears to a considerable extent during processing and that the last traces disappear within a few days thereafter. This belief has led some to infer that the possibility of oxygen being an important factor in causing perforations is rather slight, although it is admitted that before the oxygen disappears it may start some activity which continues after the last trace is gone. The disappearance of oxygen soon after processing has been generally considered to be due to its combining with some constituent of the food.

In order to obtain more definite knowledge bearing on these questions, apples were canned under three sets of conditions so as to bring about a variation in the oxygen content. They were packed in No. 2 enameled cans, all of which were made from the same base plate.

In Experiment 1 the apples were put into the cans, which were placed under a bell jar and subjected three times to a vacuum of approximately 27 in.; each time the vacuum was released with nitrogen. The cans were then filled with boiling water, exhausted in boiling water for 2 min., closed, processed in boiling water 6 min., and cooled.

In Experiment 2 the apples were also evacuated three times, but in this case the vacuum was released with oxygen, and thereafter the cans were filled with water through which oxygen had bubbled for 1 hr., and which was then heated to 60° C. The apples in this experiment were also given an exhaust of 2 min., but they were processed 8 min. to make up for the lower temperature of the filling water. Under these conditions the gas in the cans at the time of closure was about 80 per cent oxygen, as against 14 per cent when apples are normally canned (Table I).

In Experiment 3 the procedure was identical with that in Experiment 2 except that the exhaust was omitted and that the process was 10 min. to make up for the lack of exhaust.

The cans in these three experiments, about 30 in each, were held in an incubator at approximately 35° C. The first examination was made 6 wks. after they were canned. There were no perforations among the cans in Experiment 1, whereas among those in Experiment 2, 35.7 per cent were perforated; of those in Experiment 3, 57.6 per cent were perforated. At the end of 10 wks., 50.0 per cent of the cans of Experiment 2 were perforated, and 69.7 per cent of the cans in Experiment 3, while there was still no perforation from Experiment 1. Since apples have a pH of about 3.4, this marked effect of oxygen is not in agreement with the views recently expressed by Wilson.[3]

[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] Kohman, This Journal, 15 (1923), 273.

[3] This Journal, 15 (1923), 127.

Table I—Gas in Canned Apples

No.	Days Canned	Gas in	N_2/O_2	Per cent CO_2	Per cent O_2	Per cent N_2	Volume-Cc. CO_2	Volume-Cc. O_2	Volume-Cc. N_2
				Normal Apples—Enameled Cans (No. 2)					
1	..[a]	Total can	5.2	9.9	14.5	75.6	3.1	4.6	24.1
2	..[a]	Total can	4.9	11.2	14.0	74.8	4.4	5.8	28.7
3	..[b]	Total can	5.7	12.5	13.0	74.5	10.1	6.8	38.6
4	..[b]	Total can	6.5	12.8	11.7	75.6	2.2	1.9	12.6
5	3	Total can	5.8	9.5	13.2	77.3	4.7	6.5	38.0
6	6	Total can	7.0	11.9	11.1	77.0	6.3	5.9	40.7
7	9	Headspace	*9.8*	*9.7*	*8.3*	*82.0*	*0.7*	*0.5*	*5.5*
		Contents	*7.6*	*13.0*	*10.2*	*76.8*	*6.5*	*5.1*	*38.3*
		Total can	7.8	12.6	10.0	77.4	7.2	5.6	43.8
8	9	Headspace	*9.3*	*8.9*	*8.9*	*82.2*	*0.7*	*0.8*	*6.8*
		Contents	*5.2*	*6.4*	*15.0*	*78.6*	*3.4*	*7.8*	*40.6*
		Total can	5.6	6.8	14.1	79.1	4.1	8.6	47.4
9	34	Headspace	*12.5*	*5.0*	*7.5*	*87.4*	*0.8*	*1.1*	*12.8*
		Contents	*10.3*	*14.7*	*7.6*	*77.8*	*6.0*	*3.0*	*31.2*
		Total can	10.6	12.1	7.6	80.4	6.8	4.1	44.0
				Normal Apples—Plain Cans (No. 2)					
10	2	Headspace	*15.1*	*5.0*	*5.9*	*89.1*	*0.6*	*0.6*	*9.7*
		Contents	*23.5*	*10.3*	*3.7*	*86.0*	*2.9*	*1.0*	*23.6*
		Total can	20.2	8.8	4.3	86.9	3.5	1.6	33.3
11	3	Headspace	*0.0*	*6.7*	*0.0*	*93.3*	*0.4*	*0.0*	*6.4*
		Contents	*71.8*	*9.1*	*1.3*	*89.6*	*2.7*	*0.3*	*26.2*
		Total can	89.3	8.6	1.0	90.4	3.1	0.3	32.6
12	3	Headspace	*110.0*	*5.9*	*0.8*	*93.3*	*0.7*	*1.1*	*10.0*
		Contents	*75.3*	*13.3*	*1.1*	*85.6*	*4.3*	*0.3*	*27.5*
		Total can	82.2	11.5	1.1	1.1	5.0	0.4	37.5
13	13	Headspace	*0.0*	*1.2*	*0.0*	*98.8*	*0.1*	*0.0*	*7.3*
		Contents	*81.3*	*15.2*	*1.0*	*83.8*	*5.4*	*0.4*	*29.5*
		Total can	101.0	12.8	0.9	86.3	5.5	0.4	36.8
14	13	Headspace	*0.0*	*6.8*	*0.0*	*93.2*	*0.9*	*0.0*	*12.4*
		Contents	*47.5*	*25.1*	*1.5*	*73.4*	*5.9*	*0.4*	*17.2*
		Total can	81.5	18.5	1.0	80.5	6.8	0.4	29.6

[a] Immediately after closing without processing

[b] Immediately after processing and cooling.

In work of this kind there are always a number of uncontrollable variables, and it is questionable how far conclusions should be drawn. However, the results were so striking that they suggested further studies. Apples were therefore canned with their normal gas content in plain and enameled cans, and the gas in the cans was analyzed from time to time. The results of the analyses are given in Table I. Determinations were made between the intervals given, but are omitted to conserve space.

These figures indicate that the disappearance of oxygen in a can is due, in the case of apples, largely to its combination with the tin plate rather than with the food product. This agrees with the fact that oxygen does not disappear rapidly in enameled cans, as well as with the fact that some oxygen still remains within the apples in plain cans even after 2 wks., although the oxygen was all gone in the head-space after about 3 days. If this view is correct, it offers a plausible explanation for the fact that enameled cans tend to perforate far more than plain cans. It indicates that the length of time that the oxygen remains in enameled cans is proportional to the completeness with which the tin plate is protected by the enamel. The most efficiently enameled cans would therefore not only contain oxygen for a greater length of time, but would have it in greater concentration. Moreover, all the oxygen would be available for the small exposed areas of the tin plate.

If we assume that the process of enameling does not bring about a change in tin plate which increases its tendency to perforate, and that the enamel is inert in this respect, then the various facts about perforation can best be explained by assuming that it is largely influenced by some substance whose quantity is limited and at times is present only in negligible amounts. We know of no other substance that fits into this condition quite as well as oxygen, although we do not wish to imply that oxygen is always necessary for perforations to occur. We have no more evidence for this assumption than for a contrary one, yet it offers a suitable working hypothesis to follow out the ideas suggested herein.

In considering these data, it should be kept in mind that apples are a porous product and by virtue of this condition more gas is occluded than in many other fruits. This may have some bearing on the fact that apples perforate even in plain cans. Approximately one-fourth of the volume of the apples used in these experiments was gas. For this reason no allowance was made for headspace, but instead the cans were filled to overflowing. During processing and cooling part of the gas escaped from the apples to form a headspace. This difference in physical condition of the various fruits is a factor in determining the amount of oxygen that is carried into the can.

Finally, the possibility should be kept in mind that some fruits may contain substances which augment certain reactions, but which are not found in other fruits. We need not limit such possibilities to thermolabile substances like the enzymes, since Hopkins[4] has found in yeast and animal tissues a thermostable substance, glutathione, which acts as an oxidation-reduction system.

Conclusion

Although oxygen in canned apples disappears within a few days after canning in plain cans, in enameled cans it disappears only slowly. This indicates that its disappearance is due to its action on the tin plate rather than a combination with the apples, and is offered as a tentative explanation for the fact that enameled cans perforate more rapidly than plain cans. Oxygen obeys the law of mass action in causing perforations rather than acting as a catalytic agent.

[4] *J. Biol. Chem.*, **54** (1922), 527.

Briquetting. By Albert L. Stillman. 466 pp. 159 illustrations. The Chemical Publishing Co., Easton, Pa. Price, $6.00.

This book is very welcome to any one interested in briquetting, as it gives an excellent picture of American practice and experience. It is well written, well printed, well illustrated, and well indexed. It tells about briquetting fuels, ores, by-products, and metal scrap. The several types of briquetting presses are tersely presented. The story of briquetting steel swarf, turnings, and cast-iron borings is interestingly told, and will be new to many, as will the similar briquetting of light brass and bronze.

The chapter on binders is sufficiently comprehensive to show the great variety of materials proposed for use, and the limitations of each. There is a short but interesting chapter on briquetting wood waste. The author is cautiously optimistic in his treatment of peat briquetting, the chapter giving an excellent picture of the development of peat, fuel utilization in America.

The treatment of the subject of briquetting of lignite or "Braunkohle" would be improved by bringing out more sharply the distinction between American lignite and German "Braunkohle." The assumption that our lignite is the equivalent of German "Braunkohle," and therefore to be treated by the same process has led to much waste of money. The chapter is, however, a valuable resumé of the efforts that have been made to improve lignite as a fuel. A readable chapter on the principles of briquetting binders helps to dispel any thought that sticking coal particles together with pitch is a simple art. A history of fuel briquetting in the United States and Canada is given to show the difficulties to be avoided in future construction. The many projects are briefly mentioned, and the causes of failure or success indicated. The metallurgist will be interested in the chapters on flue dust and ore briquetting.

At the end of each chapter is a comprehensive bibliography of the subject, and there is a better-than-usual index at the end of the book.

The book is an excellent addition to descriptive technical literature, and should be read by everyone interested in any way in briquetting.

O. P. Hood

Division of Biological Chemistry

The division of biological chemistry devoted the entire program on Thursday to the symposium on nutrition. The room was packed to capacity the entire day and those in attendance seemed to agree that it was the most interesting and beneficial symposium that they ever attended. Two ideas stood out very prominently in the discussions. The first was that faulty nutrition during the past few years is very largely responsible for the rapid increase of all kinds of nervous disorders, the rapid increase in the decay of the teeth, and the rapid increase in the various reproductive disorders among the American people. The other point brought out in the discussions was that most of the manufacturers of foods, such as the bakeries, the canneries, cereal-food producers, milk condensers, etc., are making every effort now to put into the dietary of the American people those substances which are known to be essential to health.

J. S. Hughes, *Chairman*

The Development and Use of Standards for Reagent Chemicals[1]

By W. D. Collins

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PUBLICATIONS on the subject of standards for reagent chemicals have necessarily followed in a general way the work of Krauch, published in 1888, and revised in 1891 and in 1896. The publication issued by E. Merck, of Darmstadt, in 1905, and revised in 1912, was a continuation of the series, as is Murray's "Standards and Tests for Reagent Chemicals," published in 1920. This last book is not a mere revision of the earlier ones, but is the product of the author's years of experience in charge of the control laboratories of Merck & Company, at Rahway, N. J. The close connection of these later publications with the firms of E. Merck, at Darmstadt, and Merck & Company, of New York, has limited their usefulness as avowed reference standards for other manufacturers of chemicals. The Merck reagents have been sold as conforming to the standards given in these texts.

Baker & Adamson, now the Baker & Adamson Works of the General Chemical Company, of Easton, Pa., started over twenty years ago to put out a line of analyzed chemicals. Each bottle bore on the label an analysis showing the limits of strength and purity of the contents. A little later the J. T. Baker Company, at Phillipsburg, N. J., began the manufacture of a similar line of analyzed reagents. The tests used for the Baker and Adamson reagents have not been published. Those used by the J. T. Baker Company for a considerable number of their analyzed reagents have been described in different numbers of the *Chemist-Analyst*, published by the company.

More recently, Powers-Weightman-Rosengarten and the Mallinckrodt Chemical Works have developed lines of reagent chemicals with analyses and standards of purity given on the labels. The tests used by Powers-Weightman-Rosengarten have not been published. The tests employed for some of the Mallinckrodt reagents are given in the Mallinckrodt Red Book, published in 1922.

For a number of years Eimer & Amend has sold reagent chemicals which it guarantees. More recently, the Central Scientific Company has adopted the same practice. These two firms do not manufacture the reagents, but guarantee the quality on the basis of analyses made in their own laboratories. This is, in fact, the practice of manufacturers with reference to some of their guaranteed reagents.

The differences between the standards of the different manufacturers are not great. The difficulties that have been experienced in the use of these analyzed chemicals have rarely been from any laxity in the standards, but in practically all instances have been due to deficiencies in purity or strength that were so great as to suggest that testing of the particular lot in question had been omitted entirely. A number of instances of this sort are given in a paper by H. E. Buc, on the quality of chemicals received by the Bureau of Chemistry during the war.[2] Although this paper was confined to the experience of the author over a period of about four years, the record of laboratories where such tests have been made indicates that similar difficulties had been experienced before the war.

The U. S. Pharmacopeia has always given certain standards for the reagents used in testing the different substances listed. These standards have in the past generally been somewhat less severe than the standards of purity claimed for some of the analyzed reagents. It has been noted, however, that the analyzed reagents, for which much greater purity was claimed, were frequently less pure than material sold under the designation "U. S. P." This has resulted from the fact that if a chemical is purified sufficiently to pass a moderate requirement for purity, such as the older U. S. P. standards, it is considerably purer than these standards require.

A committee representing the Institute of Chemistry of Great Britain and Ireland, the Society of Public Analysts, and other analytical chemists published in 1915 a list of analytical reagents and tests. This list covered a large number of ordinary laboratory reagents. The standards and tests must have been taken in large measure from published works, and probably represented comparatively little original work done specifically for the report. The tests are not notably different from those of Krauch.

A similar report was published by a committee representing Group 1 of the "Congress de la Chimie Industrielle."[3] This publication is not very different from that of the English committee.

The Committee on Guaranteed Reagents and Standard Apparatus of the American Chemical Society published[4] in 1921 tentative specifications for four reagents. These specifications also call for about the same standards of strength and purity, and prescribe tests that are not greatly different from those in other specifications. Most of the tests for ordinary impurities have been for many years so well standardized as to leave little opportunity for originality in the devising of new tests. In a few respects, however, improvements have been made in the application and interpretation of standard tests, like the use of silver nitrate for chloride and barium chloride for sulfate.

Many specifications for reagents leave considerable doubt as to the actual purity defined by the tests that are prescribed. The requirement may be that no precipitate be formed or that only a slight turbidity shall result on addition of a reagent. The difficulties arising from this usage are discussed in an article by Arny[5] in which it is suggested that:

> Such tests could direct, for instance, that a 5 per cent solution of the salt mixed with definite amounts of the appropriate reagents and diluted to a definite volume, say 10 cc., should show no more turbidity than a 5 per cent solution of the C. P. chemical, to which has been added a definite volume of a standard solution of the impurity plus definite amounts of the appropriate reagents and diluted to the definite 10 cc. volume, the two fluids to be compared in test tubes.

It is understood that this suggestion is being followed by the committee now revising the U. S. Pharmacopeia. The same principle was used[6] by the Committee on Guaranteed Reagents and Standard Apparatus of the American Chemical Society, except that the quantity of impurity is stated as a definite weight rather than as a volume of a standard solution.

A person or organization undertaking to draw up new specifications for reagent chemicals faces an extremely difficult task.

[1] Presented with the report of the Committee on Guaranteed Reagents and Standard Apparatus at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] This Journal, **11** (1919), 1140.

[3] *Chimie & industrie*, **9** (1923), 15.

[4] This Journal, **13** (1921), 735.

[5] *J. Am. Pharm. Assoc.*, **9** (1920), 972.

[6] This Journal, **13** (1921), 948.

It must be recognized at the outset that the standards for reagents for careful, general analytical work cannot be set sufficiently high to cover all uses of reagents without making the cost prohibitive. Careful examination of the published standards and tests will reveal discrepancies between the actual limits of sensitiveness of some tests and the limits given in the texts. It may also be found that either the tests or limits for some impurities are more severe than can be met by any reagents that are obtainable commercially. On the other hand, manufacturers regularly produce some reagents of considerably higher purity than is required to pass tests that have long been recognized as standard.

In view of all that has been published on the subject and in consideration of all the work now in progress, it may be doubted whether further specifications prepared by a committee of the American Chemical Society are needed. If such specifications are merely copies of those already published, they will add little to the welfare of analytical chemists. To investigate all the requirements for a single reagent, to study the products of all manufacturers, and to work over each test to find its reliability and sensitiveness is no small task. When it is done the analyst may not be much better off. A specification accomplishes little except as it is used by a buyer to govern his acceptance of articles after they have been tested. Published specifications, definitions, and tests are only minor aids to the chemist in obtaining satisfactory reagents. Constant testing in his own laboratory is necessary unless his experience or that of others has shown that the manufacturer whose reagents he uses does not permit untested reagents to be sold under his guarantee.

For a number of years the Committee on Guaranteed Reagents and Standard Apparatus has tried to learn from members of the American Chemical Society their experiences with unsatisfactory reagents, but the instances reported to the committee have been so few that if it were not for their own experiences members of the committee would think that no reagents of poor quality were manufactured or sold in the United States. This is due in part to the fact that comparatively little testing of reagents is done in the laboratories where they are used. Making new specifications will not improve the situation in this respect.

The best way to insure freedom from analytical errors due to poor reagents is by careful testing of the reagents. The next best way is to buy reagents guaranteed by a dealer or manufacturer who has not failed to maintain close agreement between the claimed and actual standards of purity of his reagents. The second is the only practicable way for many small laboratories and is the cheaper way for almost any laboratory.

Personals

H. H. Dow, president of the Dow Chemical Co., Midland, Mich., returned recently from a trip to Hawaii, Japan, and other points of interest in the Orient.

Leroy W. Davis, formerly Cleveland representative of the Universal Packing Corp., Pittsburgh, Pa., is now employed as a chemical engineer directly connected with the sales department of the New Era Metal Products Co., Kalamazoo, Mich.

Chester H. Penning has accepted an appointment as special expert with the chemical staff of the Tariff Commission.

E. L. Rimbault, formerly reclamation manager of the National Aniline & Chemical Co., Inc., at the Buffalo plant, has been appointed manager of the Intermediates and Certified Food Color Divisions, 40 Rector St., New York City.

Milo R. Daughters, manager of research for The Dominion Canners, Ltd., Brighton, Ontario, has resigned to engage in business with the Polk Co., Haines City, Fla.

Merrill A. Youtz, formerly of the Research Laboratory of Applied Chemistry, Massachusetts Institute of Technology, Cambridge, Mass., has accepted a position in the research laboratory of the Standard Oil Co., Whiting, Ind.

R. P. Rose, chemical engineer for the U. S. Rubber Co., returned to this country the first of February after having spent two years in Sumatra, D. E. I., where he installed plants for the utilization of the Hopkinson process for producing rubber and equipment for the shipment of latex to this country in ship's tanks.

C. Everett Smith, until recently a graduate student at the University of Wisconsin, has accepted a position as chief chemist for the Minnesota Mining & Manufacturing Co., St. Paul, Minn., makers of sandpaper and coated abrasives.

W. F. Lantz has been appointed chief chemist at the plant of the Bethlehem Steel Co., Bethlehem, Pa.

E. C. Moffett, formerly with the Ideal Disinfectant Corp., Woodbridge, N. J., is now in charge of the research laboratory of the American Cyanamid Co., Warners, N. J.

The division of chemistry and chemical technology of the National Research Council, Washington, D. C., has named **James R. Withrow** as chairman of the National Research Council Committee on the Use of Sodium Compounds as a Substitute for Potassium Compounds, both in Scientific and Industrial Work. Professor Withrow declined the position as chairman of this committee four years ago because of the pressure of university work.

G. F. Moulton has resigned his position at the Bureau of Standards to accept a place as chemist in the research department of F. C. Huyck & Sons, Albany, N. Y.

I. Joseph Farley, formerly an assistant examiner in the U. S. Patent Office, and a member of the District of Columbia Supreme Court and Court of Appeals Bar, has joined the staff of Richards & Geier, patent and trade-mark attorneys, 277 Broadway, New York City.

F. W. Willard has been appointed superintendent in charge of chemical engineering, development, and research for the general Manufacturing Department of the Western Electric Company's Hawthorne Works, Chicago, Ill.

L. E. Wemple, general manager of the American Zinc Oxide Company and the American Zinc Sales Co., subsidiaries at Columbus, Ohio, of the American Zinc, Lead & Smelting Co., has resigned his position to accept the position of vice president and production manager of the Evans Lead Co., Charleston, W. Va.

E. N. Klemgard, formerly chemist and lubrication engineer for Fiske Brothers Refining Co., is at present employed as chemist in the research laboratories of the Standard Oil Co., Richmond, Calif.

H. A. Noyes, formerly chemist in the Department of Agriculture, East Lansing, Mich., is now associated with R. F. Bacon at the New Rochelle Research Laboratories, 24 Grove Ave., New Rochelle, N. Y.

Arthur H. Huisken, formerly employed as chemist in the Chemical Warfare Service located at Edgewood Arsenal, Edgewood, Md., has accepted a position as chemical engineer in the Chemical Division of the Western Electric Co., Chicago, Ill.

Wilson H. Low, for twenty years head chemist of the Cudahy Packing Co., Omaha, Neb., is now employed by the Western Chemicals, Inc., at Alum, near Blair Junction, Nev.

Charles Moureu has been elected president of the Chemical Society of France.

George de Wyss has resigned his position as chemist with the Cudahy Packing Co., Omaha, Neb., to accept a position in the Research Laboratory of the Viscose Co., Marcus Hook, Pa.

W. Nelson Smith, consulting electrical engineer of the Winnipeg Electric Railway Co., and **John W. Shipley**, professor of chemistry at the University of Manitoba, have recently been awarded the Plummer Medal for 1921–22 by the Engineering Institute of Canada, for their two research papers entitled, "The Self-Corrosion of Cast Iron and Other Metals in Alkaline Soils," and "The Self-Corrosion of Buried Lead Pipes." These papers were published in the *Journal of the Engineering Institute of Canada*, in October, 1921, and June and July, 1922; and were also reproduced in full in the *Sibley Journal of Engineering*, published at Cornell University in March and November, 1922.

AMERICAN CONTEMPORARIES

Frank Wigglesworth Clarke

If at one of the SOCIETY meetings you should note in the lobby a man about five feet five inches in height, one hundred and ten pounds in weight, with pale blue eyes, little hair and most of that under his ears, chewing his finger nails and apparently absorbed in thought, though really most alert, and if on engaging him in conversation you find he speaks in a low tone with a well-modulated and quite agreeable voice, using very well-chosen language, talking good sense, but with a mild undertone of gaiety, and you find him bright and entertaining and then you find him clever, he is probably Frank Wigglesworth Clarke, known wherever the masses of the atoms are considered or the chemistry of the universe is studied. Should you join him at lunch and when the waiter has served the butter this man has said, "Take it away, please," and of the potatoes, "Take that away also," and should he be eating of sweet potato and some one has remarked to him, "Why I thought you did not like potatoes," he replies, "This is not potato, it is convolvulus," then he surely is Clarke.

FRANK WIGGLESWORTH CLARKE

A rhymster of no mean facility, a punster—for, like Lewis Carroll, words assume to him many quaint forms and appear in many droll contexts—a gossip who not only knows "everybody" but their forebears and descendants, he is one of the men who has made conversation at the Cosmos Club famous. Singularly, possessing a most retentive memory and with ready command of all his accumulated information, Clarke never seems able to recall any but pleasant things of those of whom he speaks. In the fifty-four years of our acquaintance, during thirty of which we have been closely associated, I have never known him to say a disagreeable thing of any person. Neither have I known him to praise any man to his face, but I have frequently heard him speak in high terms of praise of an absent man, and I know that many a man has secured advancement in his profession through Clarke's recommendation, though the beneficiary has rarely known of Clarke's part in the affair.

During all these years I have never known Clarke to laugh heartily, though he has frequently rippled, almost silently, at a display or thought of wit or humor. Though rarely I have seen him vexed, I have never seen him angry. In fact, I believe if he were to find himself angry he would be thoroughly ashamed of himself, and no other punishment could be so severe to one of his breeding. He likes to be at the Club as the papers are brought in, and he has sometimes gotten on the nerves of the attachés of the Scientific Library by waiting around for the opening of the periodical mail, but his eagerness seems partly due to his Sybaritic liking for the freshly calendered sheet and partly to his preferring to tell the news rather than have it told to him—thus running true to form, for it's an old saying, "You can always tell a Harvard man but you can't tell him much."

He is an amusing entertainer; no meeting of the Y. M. C. U. or of Section Q of the A. A. A. S. was complete without a "number" from Clarke. His mosquito made even Howard "sit up and take notice." He is fond of botanizing and he eagerly pursues the elusive mushrooms to their lairs and devours them. "The Obituary of an Undertaker" in *Life*, and the "Mormon Widow's Lament" in *The Galaxy* are examples of his style at odd moments.

He early began to emerge into prominence, so we find a record of him in Appleton's "Cyclopaedia of American Biography," the first issue of "Who's Who in America," the first edition of "American Men of Science," and other of the biographical publications known to the elders. Together with Ben. Franklin, Chauncey Jerome, and other Yankees, lauded in my youth for their development of the system of interchangeable parts in mechanisms, Clarke was a pioneer efficiency expert (though modern engineers believe they discovered the genus because they wrote the label), for over forty years ago he had begun testing men's work by the theory of probabilities and the method of least squares. He was the first to present a consistent theory of the evolution of the elements which has withstood all subsequent developments.

Clarke has had many unique experiences. For ten years he constituted the entire membership of our SOCIETY's Committee on Atomic Weights, created in 1892, from which, in 1902, grew the International Committee, over which he has ever since presided. He is probably the only American and certainly the only Unistatian who has been invited to deliver a Memorial Address before The Chemical Society, and his Dalton address is a model of its kind. His "Data of Geochemistry" is much more widely sought than any other of the upwards of two thousand different publications issued by the United States Geological Survey. His "Constants of Nature" were among the earliest of these records and he did them "all on his own."

Definite, systematic, original, and industrious, his output in contributions to chemistry has been large and of high quality. He has received well-deserved recognition. He is the recipient of honorary degrees from several universities, foreign and American, is Chevalier of the Legion of Honor, Wilde medalist, associate of foreign societies, and member of the National Academy of Sciences. He has conferred distinction on his profession and on this SOCIETY of which he was president.

CHARLES E. MUNROE

Calendar of Meetings

American Electrochemical Society—43rd Semiannual Meeting, New York City, May 3 to 5, 1923.

American Association of Cereal Chemists—9th Annual Convention, Sherman Hotel, Chicago, Ill., June 4 to 9, 1923.

American Leather Chemists' Association—20th Annual Meeting, White Sulphur Springs, W. Va., June 7 to 9, 1923.

American Institute of Chemical Engineers—Summer Meeting, Wilmington, Del., June 20 to 23, 1923.

American Society for Testing Materials—26th Annual Meeting, Atlantic City, N. J., week of June 25, 1923.

SCIENTIFIC SOCIETIES

A. C. S. Division and Section Reports

DIVISION OF AGRICULTURAL AND FOOD CHEMISTRY

The Division of Agricultural and Food Chemistry held a very successful meeting. All papers on the program except six read by title were presented in full or in abstract. The symposium on insecticides and fungicides arranged by T. C. Cook was a great success. A number of noted botanists and entomologists attended the symposium and took part in the discussion. A committee appointed to consider the advisability of repeating such a symposium reported favorably, and its recommendation to hold a similar meeting one year hence was adopted. C. C. McDonnell, O. Butler, and A. Kelsall were appointed a committee to assist the regular officers in the preparations for that meeting. The four papers on jellies drew a large number, who took part in an animated discussion, showing the interest in the subject at this time. This division expects to hold a one-day symposium with the Division of Fertilizer Chemistry on the subject "Fertilizers and Crops," and a shorter symposium on baking, under H. E. Barnard with the Division of Industrial and Engineering Chemistry at the Milwaukee meeting, which will leave only one-half day for general papers. It is estimated that 125 different individuals attended our sessions.

The Insecticide Symposium emphasized the great number of problems confronting the agriculturist and the great necessity for devising means for controlling various pests.

C. S. Brinton, *Secretary*

DIVISION OF CELLULOSE CHEMISTRY

The big feature of the division was the address of J. C. Irvine in which he reviewed and summarized his brilliant work on the polysaccharides. H. Hibbert presented some of his latest work on the constitution of cellulose and outlined some proposed similar work on lignin. Several papers from the Forest Products Laboratory gave the results of recent work on pulp and paper, wood distillation, wood analysis, and wood hydrolysis. The symposium on oxycellulose, cellulose hydrate, and hydrocellulose was opened by L. Wise with an excellent resumé of the subject which served as a basis for general discussion.

The Committee on Standard Cellulose presented a report which will soon be printed.

L. F. Hawley, *Secretary*

DIVISION OF CHEMISTRY OF MEDICINAL PRODUCTS

Seven very interesting papers were read and one paper was read by title at the meeting of the Division of Chemistry of Medicinal Products in the Sterling Laboratory on Thursday morning. The meeting was presided over by Chairman Edgar B. Carter. Secretary E. H. Volwiler was unable to be present at the meeting.

Several interesting developments were brought out in the reading of the papers, among them the fact that benzyl compounds do not have the specific effect which has been widely attributed to them recently as a result of the experiments of David I. Macht. The statement that the effect of the benzyl radical was no more specific, from a medicinal standpoint, than the ethyl radical in organic compounds was brought out by Oliver Kamm, who took issue with Macht's findings on the subject.

Another interesting development was the work of Allan W. Rowe and E. P. Phelps, outlined in their paper entitled "Analytical Procedure for the Quantitative Determination of Peroxide and Aldehyde in Anesthetic Ether." The authors called attention to the fact that there had been numerous untoward results from the administration of ether for anesthetic purposes, and that the disturbing factor seemed to be the aldehyde formed in the ether by oxidation. Their findings showed that peroxides and aldehyde develop particularly when the ether is exposed to light and air or is kept in metallic containers. When kept in amber-colored bottles, well stoppered and away from light, there is less possibility of oxidation.

Arthur D. Holmes contributed a very interesting study of the vitamin content of cod-liver oils. He indicated in this paper that it is possible to estimate vitamin A quantitatively by the effect on rats fed with a cod-liver oil diet.

A paper on "Pharmacological Studies of Some Aromatic Alcohols and Aldehyde Alcohols," by Arthur D. Hirschfelder and Herman H. Jensen, covered a complete line of experiments designed to prove or disprove the medicinal value of certain groups and radicals when introduced into molecules of compounds of known medicinal value.

A paper on "Some New Derivatives of Suprarenine" was presented by Casimir Funk and Louis Friedman, indicating further work on synthetic adrenaline.

B. T. Fairchild presented a paper on "The Pancreas Gland—The Research and Applied Chemistry of Its Enzymes and Internal Secretion Principles." In this paper Mr. Fairchild reviewed much of the literature on the secretions, enzymes, and hormones found in the pancreas gland, showing how a great deal of work by various research workers had been contributed long before the announcement of the discovery of insulin for the treatment of diabetes. He questioned the advisability of the issuance of a patent on a product of this kind, which had been engaging the attention of medical scientists for many years in one form or another and was really not a new product. The paper by A. W. Dox and Lester Yoder, on "Dialkyl Barbituric Acids with Tertiary Amino Grouping," and the paper by Bernard Salkin, on "The Constitution of Neoarsphenamine—A New Structural Formula," which was read by title, concluded the session.

Robert P. Fischelis

DIVISION OF DYE CHEMISTRY

The symposium on "The Coal-Tar Industry in the United States Prior to 1914" brought forth some very interesting papers and discussions. It was pointed out that the birth of the industry was in the early sixties of the last century.

The second part of the program embraced the more strictly scientific papers dealing with the analysis, manufacture, and use of dyes and intermediates.

The action of the Secretary of Agriculture in officially appointing the members of the Dye Division's Coöperation Committee as "collaborators" was described. It is hoped that this committee will help to bring the Color Laboratory of the Bureau of Chemistry and the dye industry into close and sympathetic touch for the solution of the general problems of the industry. The members of this committee are C. G. Derick, L. A. Olney, W. J. Hale, W. H. Watkins, and R. Norris Shreve.

R. Norris Shreve, *Secretary*

DIVISION OF INDUSTRIAL AND ENGINEERING CHEMISTRY

During recent years it has become the custom of the Division of Industrial and Engineering Chemistry to hold a symposium upon some practical phase of chemistry. Here fundamental and often widely scattered information is brought together. At this meeting a symposium was arranged under the title of "Materials of Chemical-Equipment Construction." P. A. Singer was chairman and arranged a very complete and comprehensive program, but unfortunately, due to illness, was unable to be present to preside. However, H. Perlstein, his associate in business, took charge of the program of the symposium.

Data concerning resistance, wearing and working properties of construction materials, and the suitability of various materials for equipment construction, are widely scattered through the literature, and to some extent inaccessible to the average chemist and chemical engineer. The papers presented brought together in convenient form some of the more recent data and reviewed some of the important materials. Much keen interest was displayed, as evidenced by the discussion following the various papers. In several instances the discussion was very spirited, especially concerning the papers dealing with corrosion and enameled apparatus. The remarks clearly showed that chemists want fundamentals to govern results rather than statements based upon empirical decisions and methods.

The general part of the program contained some papers which were of extreme value to the industrial chemist and manager. Chas. H. Herty, in his discussion concerning "The Part that Synthetic Organic Chemicals Play in the Industrial Life of the Nation," clearly showed what wonderful strides have been accomplished by the chemical industry during the last few years. It was also pointed out that various forms of insidious propaganda were being broadcast throughout the nation against the very heart of our science under various guises.

Several members were disappointed in not being able to hear the paper on "Safety and Efficiency in the Chemical Industry," but at the last moment the author was unable to attend.

Following the presentation of the paper by H. N. Holmes there was a discussion of a much advertised colloid mill which has not as yet become available to industries in this country. This was the point of most interest in the whole program.

The attendance was very good, being about 100 for most of the papers, but reaching over 300 at the time of the colloid-mill discussion.

The colloid section of the Physical and Inorganic Division joined with our division for the papers by Holmes and Bingham.

At the annual meeting in Milwaukee next September, the division will hold a symposium upon industrial chemistry as applied to the baking industry. The first half day will be devoted to this and the Division of Agricultural and Food Chemistry will meet jointly with us. In the afternoon it is contemplated to join with the Section on Chemical Education at a meeting in the Milwaukee Chamber of Commerce, where a three-speaker program will be carried out to show the relation of chemical education and industrial chemistry to business in general.

At the next spring meeting, April, 1924, there will be held a symposium dealing with the subject of heat transference.

The executive committee of the division unanimously passed a resolution highly commending the editor of *Industrial and Engineering Chemistry* for the many innovations and improvements instituted in the journal, and pledged its full support to the present policies of management.

ERLE M. BILLINGS, *Secretary*

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DIVISION OF ORGANIC CHEMISTRY

The Division of Organic Chemistry met on Thursday morning to listen to a very interesting special program on catalysis. Thursday afternoon and Friday forty-seven of the sixty-three papers were read, including those by A. F. Holleman, University of Amsterdam, and J. C. Irvine, of St. Andrews College, Scotland. The following important resolution was passed by the division:

> That no paper may be included in the program of the Organic Division unless the title is accompanied by an abstract.

A special committee was appointed to consider questions of procedure relative to the programs for the general meetings.

R. R. RENSHAW, *Secretary*

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DIVISION OF PETROLEUM CHEMISTRY

The meeting of the Division of Petroleum Chemistry was presided over by W. F. Faragher in the absence of the chairman, T. G. Delbridge, whose resignation was presented. The program was followed rapidly, a time limit on papers and on discussions being in operation. This permitted early completion of all business, a successful maintaining of interest in the papers, and the release of the members for attendance on the programs of other divisions. In connection with the several papers on viscosity there was a lively discussion on this topic.

The joint meeting with the Section of Gas and Fuel Chemistry to hear Atherton Seidell's account of the Liquid Fuel Congress which met recently in Paris was held with some difficulty because of delay in the arrival of the motion-picture films of the Congress, loaned by "La Société de Chimie Industrielle." The pictures were viewed next day by a diminished audience and proved very interesting.

A symposium on motor fuels was held with the Section of Gas and Fuel Chemistry.

Motor Fuel Symposium

The symposium on "Motor Fuels," held jointly by the Division of Petroleum Chemistry with the Section of Gas and Fuel Chemistry, under the chairmanship of Van H. Manning, consisted of five papers on subjects including absolute alcohol, coal tar, engine requirements, and economic and refinery problems connected with motor-fuel supply. These papers appear elsewhere in THIS JOURNAL. The discussion covered a number of interesting points, including the prevention of evaporation losses of gasoline and the inavailability of large supplies of fuels which can be used in high-compression motors. In connection with the paper on alcohol fuels it was pointed out that not all cellulosic wastes are suitable sources for alcohols, the soft woods being so far the only satisfactory materials. The value of joint meetings of divisions to consider topics of common interest was amply demonstrated.

W. A. GRUSE, *Secretary*

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DIVISION OF PHYSICAL AND INORGANIC CHEMISTRY

The Division of Physical and Inorganic Chemistry held four sessions at which 54 papers were presented. A particularly interesting paper was given by F. G. Donnan, on "Membrane Equilibria," before a joint meeting with the Division of Biological Chemistry.

No regular business meeting was held, but following a paper by W. L. Miller the division voted that John Johnston be appointed a committee of one to consider the practicality of publishing an inexpensive edition of the more important papers of Willard Gibbs, particularly that on "Heterogeneous Equilibria."

The executive committee met to consider amendments to the by-laws which it proposes to present at the Milwaukee meeting.

The chairman announced the appointment of H. S. Taylor, D. A. MacInnis, and W. D. Bancroft as a committee to bring in nominations for officers at the Milwaukee meeting.

GRAHAM EDGAR, *Secretary*

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DIVISION OF RUBBER CHEMISTRY

The late Charles Goodyear, the discoverer of the present method of vulcanization, was born in New Haven and did his experimental work there. A dinner party in his honor was held by this division and was attended by 140 members. A very fitting program in connection with the dinner was offered.

The rubber chemists have realized that for proper study of vulcanization they require extensive work on various methods of making delicate physical tests on vulcanized rubber. A number of papers and much discussion centered on refinements in our present methods of testing and many new ideas and methods were offered. This physical examination of vulcanized rubber is being extended to cover the relation of type and dispersion of compounding ingredients to the changes in physical effects produced. The nature of rubber latex, new methods of preparing rubber from latex, and the reversability of latex coagulation were also interestingly presented and discussed. Considerable attention was also paid to the latest developments regarding the chemical structure of the rubber molecule, as well as to the correlation of the structures of organic accelerators to their activity during vulcanization.

ARNOLD H. SMITH, *Secretary*

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DIVISION OF SUGAR CHEMISTRY

A program of unusual interest and diversity was offered to the members of the Division of Sugar Chemistry. The meeting was made memorable by addresses, given at a joint session with the Division of Cellulose Chemistry by J. C. Irvine, principal of St. Andrews College, Scotland, and H. I. Kendall, dean of the medical school of Northwestern University. Mr. Irvine spoke on "The Structure of the Polysaccharides." He presented remarkable experimental results and deductions obtained by the use of methylated sugars. Professor Kendall's subject was "Bacteria and Their Relation to the Sugars." He showed results obtained by a new and interesting technic to detect by the use of bacteria the presence of sugars existing in quantities as small as 0.001 per cent. He also indicated the recognition and differentiation of certain sugars by means of bacteria.

Important papers were presented on chemical-control problems in factory operation, and several new and improved types of factory laboratory apparatus were described. The subject of color removal from sugar liquors and the utilization of color measurement received much attention. Among the contributions in this field was one proposing for the first time a practical system of color classification of technical sugar products. A new subject was presented in an interesting paper on palm sugar and the sugar palms, which was fully illustrated by lantern slides. A new balance especially designed for laboratory sugar work was exhibited. The importance of more accurate ash determina-

tions on sugars was brought out by the papers presented on that subject, and resulted in the appointment of a committee consisting of J. R. Withrow, chairman, C. A. Browne, C. F. Snyder, and S. J. Osborne, to investigate this subject.

FREDERICK BATES, *Secretary*

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DIVISION OF WATER, SEWAGE, AND SANITATION

A special effort was made for the New Haven meeting to develop for the Division of Water, Sewage, and Sanitation a program of papers and topics for discussion devoted to sewage treatment. As a result four unusually interesting papers dealing with sewage problems were presented.

The paper by J. Frederick Jackson, on "Normalcy in Chemical Treatment of Sewage," reviewed the progress which has been made in recent years in sewage treatment and pointed out the necessity for a greater coördination of the efforts of chemists, engineers, biologists, and others interested in sewage disposal problems, and suggested the appointment of a committee representing the various professional societies for the purpose of considering some plan which would effect such coördination.

The paper by J. A. Wilson, "A Practical Solution of the Problem of Dewatering Activated Sludge," reported the work done at Milwaukee, in which it was shown how it is proposed to dewater winter sludge. Upon the successful solution of this problem depends the efficiency and success of the recently installed activated-sludge process. The paper elicited considerable discussion.

The paper by I. V. Hiscock, on "The Status of Laboratory Control of Water Supplies and Sewage Treatment in Large Cities of the United States in 1920," and the paper by J. W. Sale and C. H. Badger, on "Evidence of Industrial Pollution in the Estuary of the Housatonic River and in New Haven Harbor," were interesting discussions of sewage problems.

The paper by E. F. Kohman, "Phenol-Chlorine Water Pollution," discussed the possibility of disastrous results from the use of a chlorine-treated city water supply in the canning of foods.

Thirty-six persons attended the division meeting. A lively interest was shown in the entire program and several suggestions were made regarding future activities of the division.

W. W. SKINNER, *Secretary*

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SECTION OF CHEMICAL EDUCATION

The Section of Chemical Education opened its meeting on the general subject, "Research for Teachers." G. S. Counts brought out the idea that secondary education was getting away from allowing its program to be dictated by colleges. He said that from the standpoint of chemistry this called for research to determine the best content, methods, and tests to meet the capacity and interest of the secondary students. W. H. Chapin gave the results of his efforts in collecting research problems which would be fitting for teachers with limited time and equipment to devote to research. A vote was taken in favor of continuing his work with a view of publishing his findings. R. A. Baker showed in a very clear way the real difficulties in grading large classes in chemistry, and gave suggestions for solutions of the problems. Sickness prevented E. R. Glenn from giving his paper on "The Scientific Study of the Achievements of High-School Students in Chemistry."

The second general topic for discussion was "Analytical Chemistry." E. G. Mahin brought out the value of quantitative analysis in a very clear and convincing manner, while H. R. Kraybill showed the needs of students in analytical chemistry where agricultural interest predominates. The section passed a motion in favor of appointing a committee to study agricultural-chemistry interests more extensively and make a report at a later meeting. C. W. Cuno started a discussion on the necessity of more chemistry for engineers.

One of the outstanding features of the Friday morning session was the very helpful suggestions which were given to make teaching more efficient, Professors Lowy, Bigelow, Boyes, Silverman, Davison, and Turner being the principal contributors.

The Committee on Chemical Education made a report on the correlation of high-school and college chemistry. In this preliminary report the following points were made:

1—The teaching of chemistry in the high school should be encouraged.

2—Such a course should be given in high school that it will answer for students who go to college as well as for students who do not go to college.

3—A new course of chemistry must be outlined for the high school, taking into account both content and method.

4—Colleges must recognize high-school chemistry, at least to the degree of having a different course for those students who have had high-school chemistry.

The outlining of a new high-school course was considered so important and delicate a matter by the committee that they requested that three industrial men be added to the committee, and that these men be geographically distributed as are the high-school and college men on the committee. The section passed a motion in favor of such request, and it was left with the chairman to make such appointments. A more definite report of the committee will be made at a later meeting.

A. P. Sy gave the closing paper of the meeting, on "A Plea for a Pedagogical Scrap-Heap in Chemistry," which brought out much constructive criticism.

The meeting ended with the expression of many that it had been most delightful and helpful.

NEIL E. GORDON, *Secretary*

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SECTION OF HISTORY OF CHEMISTRY

Twelve papers were read. Edgar F. Smith gave a complete account of the investigations of M. Carey Lea (1823–1923), specially emphasizing the pioneer investigations—e. g., colloidal silver. Frederick H. Getman, in his paper on "J. Willard Gibbs and His Contributions to the Science of Chemistry," gave a critical estimate of the phase rule, discovered by Gibbs, and a scholarly account of the life of Yale's famous graduate. C. A. Browne, by means of lantern slides, depicted many historical details connected with the association books in the chemical library of John Winthrop, Jr. (1606–1676). C. A. Browne read two other papers; one described briefly Thomas Paine's account of an experiment performed by George Washington upon the production of marsh gas, and the other itemized the chemical books in the library of Col. William Bird, of Westover, Va. Lyman C. Newell's paper on the "Chemist Friends of Pasteur" showed how Pasteur's brilliant work on the constitution, optical properties, and interrelation of the tartaric acid won many friends, the chief ones being Biot, Balard, and Dumas. Professor Newell also exhibited and described some unusual association books—books inscribed by Hofmann, Williamson, Faraday, Moissan, Mme. Curie, and others. Walter L. Jennings related some reminiscences of Emil Fischer; he worked with Fischer during the latter's early years in Berlin. E. H. S. Bailey's "Personal Recollection of the Sheffield Laboratory in the Early Seventies" brought back vividly the devotion of Yale's early professors. Lyman C. Newell reported that three bibliographies of portraits of famous chemists are available; information about these bibliographies can be obtained from the National Research Council, Washington, D. C. Henry Gilman, in his paper on "What Constitutes Discovery," described some work by an American chemist who anticipated Grignard. Charles W. Cuno's paper gave in detail the methods of assaying in the early fifties.

The section arranged an exhibition of portraits, autographed letters, and old books, which was visited by a great many chemists and guests.

LYMAN C. NEWELL, *Secretary*

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SECTION OF GAS AND FUEL CHEMISTRY

The general papers of the Section of Gas and Fuel Chemistry at New Haven divide themselves naturally in three groups, including four on analytical methods, one dealing with coke-oven tar, and two dealing with thermal phenomena. The article on "The Viscosity of Coke-Oven Tars and Soft Pitches," by W. J. Huff, dealt particularly with the problem of correlating viscosity of tar products with temperature. A knowledge of this relationship is very important to assist in the design of equipment for pumping and burning the heavy tar fractions and soft pitches which remain after distillation of the lighter constituents from the raw tar. This author discussed a fundamental relationship between viscosity and temperature which he has developed, and gave data of general application.

Quantitative determination of four kinds of sulfur in coke was discussed by A. R. Powell, of the Bureau of Mines, who recommends detailed analytical procedures for this work. As the article is to be published shortly, a detailed abstract is unnecessary here. C. H. Stone and E. O. Wiig discussed their experiments on a continuous determination of hydrogen sulfide in illuminating gas. Under proper conditions of concentration and temperature they find sodium hydroxide the best absorbent for use on crude

gas, but the discussion of their paper suggested the necessity of using other methods for hydrogen sulfide in purified gas in order that the small percentages of other constituents present which react with the caustic would not vitiate the results.

A simple detector for water vapor in gases was described by E. R. Weaver and P. G. Ledig, of the Bureau of Standards, who find this device very sensitive and useful up to water-vapor pressures of at least 20 or 30 mm. As the indicator adapts itself to a new condition of humidity within approximately one minute, the device can be used where instantaneous control is essential and the device is applicable in high-pressure piping as well as under low-pressure gas conditions. The device depends for its operation upon the change in the conductivity of the thin film of hygroscopic material with change in the moisture content of the atmosphere surrounding it. By proper choice of material, moisture in any gas or vapor system can be readily detected.

L. H. Milligan, of the Bureau of Mines, reported on improvements and tests of a remodeled Burrell gas indicator for combustible gases. D. W. Wilson and L. Evans, of Massachusetts Institute of Technology, Buffalo station, discussed common errors in the use and calculation of heat balances.

J. D. Davis, of the Pittsburgh station of the Bureau of Mines, reported his investigation on the heats of reaction of various coals during carbonization. He shows that the heat of reaction is endothermic when the maximum temperature is below 400° C. with most fuels, but exothermic between 400° and 700° C., and again endothermic above 700° C.

R. S. McBride, *Secretary*

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SECTION OF LOCAL-SECTION CHAIRMEN AND SECRETARIES

The meeting was held at 4:30 Thursday afternoon, and about thirty were present. Sections were represented from Colorado to the Atlantic Coast. Informal discussion occupied the attention of the group. Some of the points considered were as follows:

(1) How to secure better programs
(2) Best constitution and by-laws for each section
(3) Intersectional meetings
(4) Local-section finances
(5) Local-section and community service
(6) Gettting out local members for meetings
(7) Best means of getting members acquainted
(8) Best methods by which local members may be interested in affairs of the national Society
(9) Adding prestige to the pin

A more detailed report will be prepared and mimeographed so that copies of it may be sent to each local section. A committee of three was appointed to arrange for prominent chemists to visit the local sections. It is expected that Professor Donnan, of University College, London, and Professor Irvine, of St. Andrews College, Scotland, who will be in this country during the fall of 1924, will be able to address several of the local sections of the Society at that time.

Copies of a tentative constitution, compiled from various local-section constitutions and submitted to the secretary, were distributed to those present so that they could be taken home for consideration. At Milwaukee this matter will be taken up in detail.

Erle M. Billings, *Secretary*

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MEETING OF OFFICERS OF DIVISIONS

On Wednesday, April 4, a meeting was held of all officers of divisions who could be secured for the purpose of discussing methods of securing uniformity of procedure in the acceptance of papers, and of improving the general character of divisional programs. About two-thirds of the divisions were represented.

After some discussion it was decided to effect a permanent organization, and to elect officers to serve for the first year. R. R. Renshaw was elected chairman, and Graham Edgar, secretary. It was voted that retiring chairmen and secretaries should remain members of the group for one year, and that officers should be elected at the spring meeting of the Society, to serve until the calling together of the group at the following spring meeting.

In order to permit more careful scrutiny of papers and transfer of papers among the divisions, the following resolutions were passed:

1—That the Secretary of the Society be requested to mail the final program at least ten days before the date of the Council meeting.

2—That the final date for the acceptance from authors of titles and abstracts of papers, by secretaries of divisions, be set at least one month before the date of the Council meeting; and that the Secretary of the Society be requested to allow at least ten days between this date and the date upon which the final programs must be in his hands.

These resolutions were later adopted by the Council.

A subcommittee was appointed to consider further problems.

It was moved and passed that secretaries of divisions be instructed to inform the secretary of this group of plans for meetings, and that the secretary of this group inform the other secretaries, in order that programs may be arranged with better correlation.

Graham Edgar, *Secretary*

A. C. S. Committee Reports

COMMITTEE ON OCCUPATIONAL DISEASES AND HAZARDS IN THE CHEMICAL TRADES

As human beings we are not only deeply interested in what befalls our fellow-men, but we are also concerned with the economic aspects of the situation. The employers' liability acts passed by the legislative bodies of many states are in themselves sufficient stimuli to study ways and means to obviate occupational diseases and hazards in the chemical and allied industries. A number of organizations have committees whose function it is to gather and disseminate information on industrial accidents, hazards, and diseases, and perhaps to devise practical methods of prevention. Some of the committees work in unison with their respective organizations, while others are something apart. Each renders a report annually, and the quality ranges from good to no good.

The necessity of a good, live committee on occupational diseases in the American Chemical Society cannot be denied, and all ought to realize that a committee of the ordinary size is much too small to study properly all the hazards in our industry. A very important step was taken when the officials of the American Chemical Society made provisions for a committee on occupational diseases. The next logical step would be for the American chemical industries to lend their facilities to the committee, and others, for studying at first hand the hazards that confront the men and women engaged in the various kinds of plants.

Some still harbor the peculiar notion that a study of occupational diseases should be left entirely in the hands of the medical doctor, industrial hygienist, and sanitary engineer, but in its 1922 report your committee stressed the point that the chemist and chemical engineer were in a position to aid it very materially in the clarification of many untoward conditions existing in the chemical works. With an increase in diversity of chemicals made by American manufacturers there is bound to come an increase in number and kinds of occupational diseases. Undoubtedly, many of the conditions and diseases previously noted in Europe will occur in our own factories. Accordingly, it behooves us to become familiar with the occupational hazards noted by our predecessors, and learn how they can be most conveniently prevented.

As health is the first requisite for obtaining a maximum day's work from an employee, it should be apparent to every reflecting mind that the very basis of the chemical industry is not secure until every process carried on therein is made safe to the workman. A good workman is a healthy workman; and maximum production rests on a healthy mind and body.

One of the greatest sources of loss to any industry is sickness, greater than from industrial accidents. It is a fact that much illness can be prevented through intelligently directed efforts.

It is a well-known fact that there is a distinct relationship between occupation, illness, and mortality. Some occupations are more dangerous than others, but any one of them would be less dangerous were the workmen acquainted with the hazard involved.

The insidious substance is what troubles us most. The after effects of exposure to chemical irritants have been the basis for much litigation and speculation. One of the greatest impulses for study of chemical irritants and the after effects therefrom has come from cases of gassing from the World War. Much can be expected when these studies are completed by the Chemical Warfare Service. Some data are available now.

The least we can do for our employees is to instill in them a spirit of caution, and this must come primarily from a knowledge of the unfortunate experiences of others. In last year's report

the committee stressed the need of a set of lectures on industrial hygiene in every course on chemical engineering. Correspondence with chemists, chemical engineers, and professors of chemical engineering and industrial chemistry brought in a number of diverse replies. Most of them see the value of such a course, some think the curriculum already overcrowded, while others are of the opinion that the course should be included at all hazards.

One of the most mooted questions was the availability of suitable talent to teach the subject of industrial hygiene, especially in schools located away from medical centers. As a last resort a member of the chemistry faculty could give a course of this character, even though the first course savors of the amateur. There are only a few chemists who can resist the temptation of becoming interested in the hygienic aspects of our industry.

There is an imperative need of subjecting every applicant for work to a thorough physical examination. This should be done by a physician skilled in diagnosis for the industry in question. We need to fit the man to the industry and not the industry to the man. The process will go a great way in insuring employers against costly risks and will tell the applicant what he should not do. In the Army during the World War only 70 per cent came up to the requirements of the Selective Service Act. A periodical examination of every worker in certain plants—and perhaps in every plant—is a practice the necessity of which needs no further explanation.

What can be done through the organization of a "Safety First" department is favorably shown from a study made in a steel mill employing about 8000 men. [Van Kirk, *J. Am. Med. Assoc.*, **79** (1922), 951.] By reason of the mandatory wearing of goggles and the use of various safety devices all types of injuries are now rarely seen. In the five years covered in the report, involving the study of 25,000 cases, only 40 major injuries occurred.

In instances where the eyes are burned, either through acid or hot metal, it is a practice to send the men to the hospital at once, even when the burn is apparently a minor one. No adequate protection was found for electric flashes. The lacrimation, photophobia, etc., is usually present for twenty-four hours thereafter despite any form of treatment. The symptoms are more severe and prolonged in persons who have previously suffered from an electric conjunctivitis.

A study of acid burns of the eyes and adnexa by sulfuric acid from storage batteries is reported by Gradle [*J. Am. Med. Assoc.*, **79** (1922), 1819]. Protection can be afforded through the use of goggles. In every shop where the possibility of acid burns exists there should be on hand a large bottle of saturated bicarbonate of soda solution in sterile water. Eye cups should be at hand for applying the solution. When such an accident occurs the eye should be quickly, thoroughly, and repeatedly bathed in an eye cup filled with the solution, after which sterile borated petrolatum can be applied and the victim sent to the nearest physician.

The majority report of the Committee on Estimating Compensation for Eye Injuries of the Section on Opthalmology of the American Medical Association [*J. Am. Med. Assoc.*, **79** (1922), 1843] is instructive, inasmuch as it deals with the method of computing compensation for loss of visual efficiency, the result of eye injuries. Those of us who have had an opportunity of seeing children and adults burned and maimed with lye, especially burns of the eyes and esophagus, can lend sympathetic support to the Committee on Lye Legislation of the Section on Laryngology, Otology, and Rhinology of the American Medical Association (*Loc. cit.*). Uniform, adequate, truthful, and warning labels should be placed on all packages of lye. Special legislation is needed to bring this about since moral suasion seems to have failed. The American Medical Association committee urges that every member of the association report every case of lye burn, giving the name of the preparation causing the accident with a note as to how much, if any, warning is given on the label.

A study of the effect of gasoline fumes on dispensary attendance and factory output was made on a group of 22 persons—male and female, ranging in age from 18 to 46 years—engaged in a coupon-stamping concern. The gasoline was used for cleansing the rubber feed belts of the stamping machines.

The application of the gasoline with a cloth to the rapidly moving belt caused a pollution of the atmosphere with fumes, which was responsible for the complaints by the workers. [*U S. Public Health Reports* **37** (1922), 38.] By computation it was found that the maximum amount of gasoline that could be inhaled by each individual was about 255.5 minums in a 7-hr. work day. The gasoline fumes produced cases of mild poisoning. The substitution of the gasoline by a mixture of pure kerosene colored with alkanet and deodorized with anise oil resulted in a marked decrease in the rate of dispensary attendance and in increased production. The symptoms of gasoline poisoning are described.

The effect of breathing carbon dioxide with air was studied at the Pittsburgh Experiment Station of the U. S. Bureau of Mines. It was found that when 2 per cent of carbon dioxide was present a slight increase in lung ventilation was noted without subjective symptoms. Five per cent of carbon dioxide caused an increase of 100 per cent without symptoms; 7.2 per cent, an increase of 200 per cent accompanied by moderate perspiration and a slight fullness in the head after a 10-min. intake of the gas; 9 to 10 per cent of carbon dioxide caused a lung ventilation of 300 per cent with frontal headache, dizziness, and perspiration at the end of 10 min. Breathing 9 per cent of carbon dioxide for as long as 45 min. produced labored breathing, dizziness, headache, and marked perspiration. Work in this atmosphere was found exceedingly difficult [*J. Am. Med. Assoc.*, **79** (1922), 1483].

Under the caption of "Nitrous Acid Poisoning," McClure and Heap [*Lancet*, **202** (1922), 1142] describe poisoning of six persons from food accidently contaminated with sodium nitrate. The symptoms noted about 15 to 30 min. after eating were flushed face, dizziness, throbbing in the head, and great difficulty in breathing. Some had stomach pain, and all but one vomited. A grayish blue cast of the face and lips was also present.

The war gases have been blamed for every conceivable ailment. There is hardly an organ in the body whose abnormality has not been ascribed to gassing. While there were but 70,552 gas casualties in our Army during the entire war, the number of applications for compensation is greatly in excess of that number. Many of the claims are made in good faith, and in many instances the ailments are due to conditions unassociated with gas, or even with war conditions. Tuberculosis, for instance, according to the British report "does not develop more frequently in gas victims than in other subjects." An analogous view is held by the French, who say: "Judging from experience, it does not seem that lung lesions caused by gassing predispose to tuberculosis." The German view is similar.

The Chemical Warfare Service concludes by saying: "As to the incidence of pulmonary tuberculosis resulting from exposure to gas, it would seem that it is far from convincing that the gas played a particular role in this connection, and it is doubtful if the incidence of lung tuberculosis among ex-service men is much greater by reason of the part that gas played."

There are two elements entering into this problem—neuresthenic, where the men were gassed, usually slightly, and believed sincerely that this was a factor in their illness; and mistaken diagnosis in many cases, especially those following influenza. [Extracts from "Report on the After Effects of Warfare Gases," issued by the chief, Chemical Warfare Service, U. S. Army—the report includes data submitted by American chemical manufacturers.]

A comprehensive report by Gilchrist, chief of medical division of the Chemical Warfare Service, on "Warfare Gases," details the history, classification symptoms, pathology, and treatment. The "Medical Aspects of Gas Warfare" are also discussed by Mankin in the *U. S. Naval Bull.* **16** (1922), 641.

Gross and criminally defective working conditions in a Viennese storage battery factory were the cause of the death of two employees. These men were obliged to make a thick paste of oxide of lead for coating the grids of storage batteries. The oxide was shoveled from a barrel into an earthenware basin of a mixing machine where the lead was incorporated with sulfuric acid to make a stiff paste. The introduction of wet methods, frequent changes of gloves and aprons, and the installation of improved washing appointments were ordered by the sanitary authorities.

The danger through the use of industrial arsenic preparations is pointed out by Wilcox [*Brit. Med J.*, **1922**, II, 3217]. "Hypersensitiveness to Local Contact with Arsphenamine Producing Chronic Eczematoid Dermatitis and Asthmatic Symptoms" is reported by Klauder [*Arch. Dermatology and Syphilology*, **5** (1922), 487]. The chronic dermatitis and respiratory symptoms were obviated through the use of rubber gloves. The dermatosis following the use of cutting oils and lubricating compounds was studied by the U. S. Public Health Service [*Public Health Reports* **37** (1922), 1773] at the request of many industrial plants who had trouble in this respect. The weight of the evidence collected incriminated oils and lubricating compounds of all types carrying extraneous matter in suspension as the primary cause producing the initial dermatosis by obstruction of the sebaceous follicles, the underlying or basic cause being a deficiency of the natural oiliness of the skin. Infecting organisms which usually inhabit the body surface, but which may inhabit the cutting oils, may find ingress to the skin through the primary dermatic lesions by reason of the sufferer's scratching the affected surface or by reason of other irritation, and thereby produce a secondary infection of the dermatosis as a complication. In other cases the abrasions produced by particles of metals become infected and complicate the dermatosis. Prevention depends upon thorough cleanliness and upon the application of lanolin and castor oil to the skin at the beginning of the work period. Methods of sterilization are described.

Information like the foregoing must be brought early to the chemists and chemical engineers and in easily assimilable form. We must bear in mind the fact that most of us are neither physicians, pharmacologists, physiologists, nor industrial hygienists, but notwithstanding there is no valid reason, the committee believes, why we should not be informed precisely about the hazards which confront us in our respective endeavors. No movement like this can succeed without intelligent coöperation such as chemical engineers and chemists can give. After all, the basic data for invoking "up to the minute" preventive measures must come from those supervising our chemical plants.

Much valuable material is lost through a lack of interest because the person is usually uninformed and to get the information is rather an unwieldy task. On the other hand, the fear of a possible litigation sometimes stands in the way of looking further into the matter.

Much information has been given to the chemical industry on ways and means of correcting existing conditions in the plants, and plans for obviating them in the future. Many of the questions asked involved occurrences that are matters of repeated record. Much time could be saved if such material were made readily available to the chemist and chemical engineer through his regular literature. In this connection, the matter has been taken up with the editor of *Chemical Abstracts*, who has it under consideration. It is hoped that a special column will be set aside in our valuable abstract journal, with appropriate cross references in other sections, so that there will be a certainty of reaching all who make or use the same chemicals in their respective works.

The matter of lack of finances is still a very troublesome one. The quality of work which the committee can do is limited considerably through this deficiency. Several organizations, such as the National Research Council, Rockefeller Foundation, etc., were approached, and they have the matter under consideration, or are seeking further information as to what we propose to do in industrial hygiene.

LEWIS W. FETZER, *Chairman*

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COMMITTEE ON GUARANTEED REAGENTS AND STANDARD APPARATUS

The work of the committee on the subject of reagents has been confined to furnishing information in regard to sources of reagents and in regard to the standards of purity of reagents now on the market.

The Committee on Pure Products of Research of the International Union of Pure and Applied Chemistry is compiling data on the subject of analytical reagents, and the reports of former work of the Committee on Guaranteed Reagents and Standard Apparatus have been furnished to the Committee of the International Union. If the Committee of the International Union undertakes the preparation of standards for reagents, the American correspondent will expect the Committee on Guaranteed Reagents and Standard Apparatus to pass upon any proposed specifications on behalf of the AMERICAN CHEMICAL SOCIETY. A brief discussion of the subject of standards for reagents is published elsewhere.[1]

In general, the conditions regarding analytical reagents were never so favorable for chemists in the United States. The older manufacturers continue to improve their products and some of the newer brands of guaranteed reagents are reported to be giving entire satisfaction.

Continuing the coöperation with the Committee on Standardization of the Association of Scientific Apparatus Makers of America, recommendations have been made for the elimination of some more items from the lists in the catalogs of dealers. The lists reported in previous years,[2] with the additions made this year, are being published with illustrations by the Association of Scientific Apparatus Makers. The items were identified by catalog numbers while under consideration by the committees, but since these numbers could not well be published and it was not possible to describe some pieces satisfactorily in any reasonable space, the committee reports have not been perfectly definite to those who did not have the catalog numbers. This difficulty will be removed by the publication of the illustrations.

Through the relations established with manufacturers and dealers the committee has been able to assist members of the SOCIETY in obtaining apparatus for their special needs, and has advised manufacturers in regard to details and dimensions for pieces of apparatus. There should be a greater field of usefulness along these lines for a committee made up of members of the SOCIETY actively engaged in laboratory work at large institutions and in different fields of work.

The committee has kept in touch with the committee appointed at a conference at the Bureau of Standards over a year ago to select sizes for beakers and flasks. A final report on that subject should be issued before long.

The committee represented the AMERICAN CHEMICAL SOCIETY at a conference of Makers and Users of Scientific Apparatus held by the National Research Council, March 23 and 24, 1923.

W. D. COLLINS, *Chairman*

[1] See page 529 of this issue.

[2] THIS JOURNAL, **13** (1921), 1070; **14** (1922), 654, 738.

COMMITTEE ON INDUSTRIAL ALCOHOL

The Committee on Industrial Alcohol was started in 1921, and since then has been compelled to be on the alert watching the various factors that affect the supply and use of alcohol in legitimate industries, and extending its services where action seemed appropriate, in efforts to improve the conditions governing the regulation of industrial alcohol.

As you well know, the Eighteenth Amendment and the National Prohibition Act not only provide for the legitimate use of alcohol under reasonable regulations, but the law expressly encourages such use. Unfortunately, many of those active in the effort to enforce prohibition are not aware of the necessity of providing alcohol for industrial purposes, and there seems to be a tendency to put men of this kind in charge of prohibition enforcement.

The National Prohibition Act provides not only for prohibition enforcement, but Title 3 of this act provides with equal authority for the manufacture, sale, and use of industrial alcohol under reasonable regulations, and specifically charges the Commissioner with encouraging such manufacture, sale, and use of industrial alcohol as a chemical raw material, in every way possible consistent with the interests of the Government.

It is the opinion of those engaged in industries depending on a supply of alcohol, who are in touch with the details of the law enforcement, that the prohibition part of the law is given greater weight in enforcement than Title 3 pertaining to industrial alcohol. There is a strong and persistent demand from the industrial interests that Title 3 of the act shall be given equal recognition in enforcement.

The Committee on Industrial Alcohol was among the first to recognize the desirability and necessity of enforcing Title 3 along with the other portions of the act. The committee was also among the first to recognize the fact that a Prohibition Commissioner, who might be possessed of admirable qualities as a policing officer for enforcing prohibition, could hardly be expected to be the best man to pass on the merits of technical questions involved in the use of industrial alcohol.

Those interested in the enforcement of the National Prohibition Act find themselves almost without exception in one of two very different groups. One group seeks to concentrate all authority over alcohol in one man, a Prohibition Commissioner, who would be possessed, in effect, of legislative powers, inasmuch as regulations drawn up by him would have the force of law without requiring the consent of any other officer and would be subject only to the President; a commissioner possessed also of executive and judicial powers and whose acts would not be subject to the jurisdiction of any court for review. The other group interested in the enforcement of the National Prohibition Act views with alarm any attempt to concentrate such vast powers in the person of one man, and especially decries any move leading to the abolition of the right of appeal and of court review.

In April, 1922, two identical bills were introduced in both branches of Congress, S. 3713 and H. R. 12,035, aiming to create a Prohibition Commissioner who would be endowed with vast, sweeping, arbitrary powers, with no provision for court review. On account of the rush of important business, including tariff, bonus, etc., this bill was not given an opportunity for active consideration during the special session of Congress. Towards the end of the regular session, when there was little chance of the bill actually passing, its advocates sought a hearing before the House Judiciary Committee, at which it was aimed that only advocates of the bill might be heard, the intention being to get their arguments only into the *Record* in order to create a favorable impression for the bill that would aid its passage through the new Congress. Some of those opposed to a hearing that allowed one side only to be presented on so important a matter, including your Committee on Industrial Alcohol, on learning of the hearing sought an opportunity to present arguments against some of the features of the bill. Opponents of the bill were not heard, but a concession was made, owing to their demand whereby their written statements filed with the Committee of the Judiciary would receive consideration. The Committee on Industrial Alcohol filed a short argument against this bill without full opportunity for hearings and opposing some of the drastic features of the bill.

Of greatest importance was the presentation by C. L. Parsons of a resolution that was approved on Feb. 10, 1923, as the action of the SOCIETY, this resolution being especially pertinent to the consideration of bill H. R. 12,035. The resolution is as follows:

In order that the National Prohibition Act may be more equitably and effectively administered and that industries depending upon the use of industrial alcohol may be permitted to operate under reasonable regulations and be encouraged as expressly provided in the law, and in order that violations of the law may be more readily prosecuted the AMERICAN CHEMICAL

SOCIETY recommends that Title 3 of that act pertaining to industrial alcohol shall be given equal weight in enforcement with other portions of the act, and recommends that to this end an Industrial Alcohol Commissioner be appointed with authority equal to and apart from the Prohibition Commissioner, whose duties shall be the administration of those portions of the law pertaining to industrial alcohol.

The Prohibition Commissioner holds office as an Assistant Commissioner of Internal Revenue, and the Commissioner of Internal Revenue by the same authority which permitted him to appoint a Prohibition Commissioner would be empowered to appoint a coördinate officer, an Industrial Alcohol Commissioner. This latter officer might best be a technical man, and in any case should have technical men on his staff. Such an officer could give the proper attention to Title 3 that this important part of the law demands. He could give intelligent and impartial consideration to each application for a permit to use alcohol, to the end that legitimate users of alcohol could get their supplies with the minimum amount of difficulty and the bootleggers would the more readily be recognized and differentiated against.

On March 21, 1923, the committee presented to the Commissioner of Internal Revenue in Washington the resolution of the SOCIETY, and argued in favor of the resolution and an impartial enforcement of the industrial alcohol portion of the law. The Commissioner evinced great interest in the part the SOCIETY is taking in this important matter and after the statements and arguments had been presented, the Commissioner signed an order creating an advisory board to be made up of men drawn from our SOCIETY and from the alcohol-using industries, to which board important matters pertaining to alcohol are to be submitted for an opinion before action is taken on them. This is a move in the right direction and of great importance to all concerned.

The committee has pursued a consistent policy, that as long as it exists it shall be a real committee. While it is in no way interested as a committee in the principle of prohibition either for or against, it is very much interested in Title 3, the industrial-alcohol portion of the act, and stands unequivocally for that impartial law enforcement that would handle industrial alcohol as it should be handled.

The committee has avoided all mooted questions and does not serve as a bureau for ordinary complaints.

It has been practically unanimous in all that it has done, and so far as it has been able to learn, its action has met with the enthusiastic approval of the industries. The resolutions adopted by the SOCIETY have been especially well received both by the Government and by the industries.

If one is ever justified in prediction, we might well conclude that for some time to come the efforts at enforcing prohibition will involve the manufacture and use of industrial alcohol, and that industrial alcohol will be subjected to serious buffeting and many unreasonable restrictions unless the men of science and of industry who are aware of its importance are ready to demand for it the rights that it should enjoy in the impartial enforcement of just laws.

MARTIN H. ITTNER, *Chairman*

Effect of Integral Waterproofing Compounds on the Strength of Concrete

Editor of Industrial and Engineering Chemistry:

In a paper on "Integral Waterproofings for Concrete" in THIS JOURNAL, 15 (1923), 150, Prof. Alfred H. White stated that in some instances there was an increase in strength of concrete due to the use of integral waterproofing compounds. As a part of a general investigation of the effect of alkali on concrete being carried on in this laboratory, we recently made compression tests of 6 by 12-in. concrete cylinders, in which eleven different integral waterproofing compounds were used in 1:3, 1:4, and 1:5 concrete mixtures, with aggregate graded up to 1.5 in. In a number of instances two or three percentages of the compounds were used. The tests were made after curing the concrete 28 days in a moist room. "Normal" concrete—that is, without integral compounds, gave the following strengths—1:5, 3010; 1:4, 3460; and 1:3, 4230 lbs. per sq. in.

Without exception the compressive strength of the concrete was reduced by these compounds. A soap solution of $^1/_4$ lb. per gal. of mixing water gave a concrete strength 57 per cent of normal; 5 per cent crude oil (both asphaltic and paraffin base) gave concrete strengths 73 per cent of normal.

Four different proprietary waterproofing compounds, used in the percentages recommended by the manufacturers, gave concrete strengths 74 to 87 per cent of normal—average, about 80 per cent. A so-called "alkali-proofing" compound (patented) gave concrete strength 16 per cent of normal.

Little difference was found in the relative effect of integral compounds due to the quantity of cement within the range of the mixes used in these tests.

We have made no tests on the value of these compounds for waterproofing, and at this time no conclusions can be given with reference to their effect in concrete exposed to alkali. However, users of such compounds should consider that the strength and probably the resistance of the concrete to destructive agencies may be seriously reduced thereby.

The Progress Report of the Joint Committee on Standard Specifications for Concrete and Reinforced Concrete treated this phase of waterproofing concrete very briefly by saying that "integral compounds shall not be used." This committee is composed of five representatives from each of five of the leading American engineering organizations that are interested in this field. Their report was published in 1921 by the American Society of Civil Engineers and by the American Society for Testing Materials.

D. A. ABRAMS

STRUCTURAL MATERIALS RESEARCH LABORATORY
LEWIS INSTITUTE, CHICAGO, ILL.
February 8, 1923

Tenth Annual Report on the Industrial Fellowships of Mellon Institute

The Tenth Annual Report of the Mellon Institute of Industrial Research of the University of Pittsburgh covers the work of the Institute for the fiscal year ended February 28, 1923.

The Industrial Fellowships of the Institute are of two general types—viz., individual and multiple. An Individual Industrial Fellowship utilizes the services of one research chemist or engineer (with assistants when necessary), who is responsible directly to the executive staff of the Institute. A Multiple Industrial Fellowship has the services of one or more research men (Junior Fellows) under the direction of a Senior Fellow, who, in turn, is responsible to the executive staff.

At the end of the Institute's fiscal year, fifty Industrial Fellowships were in operation, employing eighty research chemists and engineers. The sum of $351,049.30 was contributed for the support of this work by the Industrial Fellowship donors. Two additional Fellowships have been accepted, to begin on May 1, 1923.

The total amount of money donated by industrial firms to the Institute for the twelve years ended March 1, 1923, was $2,306,-971. During the same period the Institute itself expended $481,-100 in taking care of overhead expenses—salaries of members of

INDUSTRIAL FELLOWSHIPS IN OPERATION AT MELLON INSTITUTE ON MARCH 1, 1923

Nos.	Names of Industrial Fellowships	Industrial Fellows, Names and Degrees	Dates of Expiration
181	Synthetic resins	*C. B. Carter* (Ph.D., University of North Carolina), senior fellow	May 1, 1923
		A. E. Coxe (B.S., University of Chicago)	
309	Glue	A. M. Howald (Ph.D., University of Pittsburgh)	April 1, 1923
324	Textile	E. R. Clark (B.A., Yale University)	April 1, 1924
326	Enameling	R. D. Cooke (M.S., University of Wisconsin)	April 1, 1923
327	Varnish	Marc Darrin (M.S., University of Washington)	May 1, 1923
328	Steel	B. B. Wescott (Ph.D., University of Pittsburgh)	June 15, 1923
329	Stove	J. E. Hansen (B.S., University of Illinois)	June 22, 1923
330	Bread	*H. A. Kohman* (Ph.D., University of Kansas), senior fellow	June 1, 1923
		Roy Irvin (M.S., University of Kansas)	
		E. S. Stateler (M.S., University of Pittsburgh)	
331	Protected metals	*J. H. Young* (Ph.D., Ohio State University), senior fellow	June 1, 1923
		P. D. Gephart (B.Ch.E., Ohio State University)	
332	Food container	*W. F. Henderson* (Ph.D., University of Pittsburgh), senior fellow	July 12, 1923
		H. E. Dietrich (A.B., University of Kansas)	
333	Corrosion	C. R. Texter (B.S., Pennsylvania State College)	July 1, 1923
334	Edible gelatin	T. B. Downey (Ph.D., University of Pittsburgh)	September 1, 1923
335	Ester	J. J. Fitzpatrick (B.Chem., University of Pittsburgh)	August 15, 1923
336	Oil	*W. F. Faragher* (Ph.D., University of Kansas), senior fellow	September 1, 1923
		W. A. Gruse (Ph.D., University of Wisconsin)	
		R. W. Henry (B.S., University of Oklahoma)	
		S. P. Marley (B.S., University of Pittsburgh)	
337	Metallic oxides	G. E. Seil (Ph.D., University of Pittsburgh)	September 1, 1923
338	Slag	*Tracy Bartholomew* (E.M., Colorado School of Mines), senior fellow	September 21, 1923
		H. C. Hoover (A.B., Ursinus College)	
339	Gas	*J. B. Garner* (Ph.D., University of Chicago), senior fellow	September 15, 1923
		Gertrude E. Price (A.B., Goucher College), assistant	
340	Wood chemicals	R. F. Remler (B.Chem., University of Pittsburgh)	November 1, 1923
341	Perfumes	L. E. Gilson (Pharm.B., University of Southern California)	October 1, 1923
		E. H. Balz (Ph.D., University of Pittsburgh)	
342	Carbon dioxide	C. L. Jones (M.S., University of Pittsburgh)	October 16, 1923
343	Pratt	*L. H. Cretcher* (Ph.D., Yale University), senior fellow	December 15, 1923
		F. W. Hightower (B.A., University of Texas)	
344	Inks	F. F. Rupert (Ph.D., Massachusetts Institute of Technology)	November 1, 1923
345	Chrysotile	Henry Joseph (Ch.E., Columbia University)	January 1, 1924
346	Laundry	*A. F. Shupp* (Ph.D., University of Pittsburgh), senior fellow	November 1, 1923
		Alice L. Wakefield (B.S., Carnegie Institute of Technology)	
		Mary M. Danley (B.S., Carnegie Institute of Technology)	
347	Emulsion flavors	Melvin DeGroote (B.Ch.E., Ohio State University)	November 15, 1923
348	Heavy chemicals	E. E. Marbaker (Ph.D., University of Pennsylvania)	December 1, 1923
349	Fiber	M. C. Walsh (Ch.E., Columbia University)	November 15, 1923
350	Salt	T. E. Williams (B.S., University of Michigan)	November 1, 1923
351	Nickel	*O. B. J. Fraser* (B.S., Queen's University), senior fellow	December 1, 1923
		H. E. Searle (B.S., Queen's University)	
352	Silicate	J. L. Crawford (B.S., University of Illinois)	December 1, 1923
353	Medicinal	C. C. Vogt (Ph.D., Ohio State University)	January 1, 1924
354	Varieties	*E. R. Harding* (M.A., Leland Stanford University), senior fellow	January 1, 1924
		F. J. Murphy (B.S., University of Pittsburgh)	
355	Fertilizer	*H. H. Meyers* (B.S., University of Pennsylvania), senior fellow	January 5, 1924
		W. T. Nichols (B.Chem., University of Pittsburgh)	
356	Insulation	R. H. Heilman (E.E., University of Pittsburgh)	January 1, 1924
357	Coke	*F. W. Sperr, Jr.* (B.A., Ohio State University), advisory fellow	January 1, 1924
		W. J. Huff (Ph.D., Yale University)	
		H. J. Rose (B.A., Yankton College)	
		J. A. Shaw (B.S., Pennsylvania State College)	
		G. G. Desy (B.S., Worcester Polytechnic Institute)	
358	By-products	Walther Riddle (Ph.D., University of Heidelberg)	January 1, 1924
		H. E. Gill (Ph.D., University of Pittsburgh), assistant	
359	Insecticides	O. F. Hedenburg (Ph.D., University of Chicago)	February 1, 1924
360	Asbestos	G. H. Katz (B.S., Ohio State University)	February 1, 1924
361	Metalware	W. G. Imhoff (M.S., University of Pittsburgh)	February 16, 1924
362	Organic synthesis	*J. G. Davidson* (Ph.D., Columbia University), senior fellow	January 1, 1924
		C. J. Herrly (B.S., Pennsylvania State College)	
		A. R. Cade (M.S., University of Minnesota)	
		J. T. Baldus (B.Chem., University of Pittsburgh), assistant	
363	Synthetic acids	R. B. Trusler (B.S., Syracuse University)	February 1, 1924
364	Dental alloy	J. W. Harsch (B.S., University of Illinois)	March 1, 1924
365	Roofing	E. S. Ross (M.S., New Hampshire College)	February 1, 1924
366	Refractories	*M. C. Booze* (B.S., University of Illinois), senior fellow	March 1, 1924
		S. M. Phelps (University of Toronto)	
		R. F. Ferguson (B.S., University of Pittsburgh)	
		Jules Labarthe (B.S., University of California)	
		W. R. Kerr (University of Pittsburgh), assistant	
367	Magnesia products	H. W. Greider (M.S., University of Kansas)	March 1, 1924
368	Pharmaceuticals	A. W. Harvey (Ph.D., University of Pittsburgh)	March 1, 1924
369	Smoke	A. R. Powell (Ph.D., University of Illinois)	March 1, 1924
370	Vitrified tile	*H. G. Schurecht* (B.S., University of Illinois), senior fellow	March 1, 1924
		G. R. Pole (B.S., University of Washington)	
371	Vitrified tile	*H. G. Schurecht* (B.S., University of Illinois), senior fellow	March 1, 1924
		G. R. Pole (B.S., University of Washington)	
372	Cleaning	*L. E. Jackson* (B.S., University of Kansas), senior fellow	March 1, 1924
		Helen E. Wassell (B.S., Carnegie Institute of Technology)	

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the executive staff and office force, maintenance of the building, purchase of books and apparatus, etc.—in connection with the operation of the Industrial Fellowships. Besides this amount the Institute has invested in a building and permanent equipment, which make it the most nearly complete and most modern industrial experiment station in the country.

Three of the Industrial Fellowships now in operation (Nos. 309, 330, and 336) have been effectively at work since 1911, while 22 other Fellowships have been promoted continuously for three or more years, and 13 Fellowships are in their second year of operation.

The following Industrial Fellowships have been founded by associations of manufacturers:

Numbers	Names	Company Members in Associations
329	Stove	15
334	Edible gelatin	7
340	Wood chemicals	68
342	Carbon dioxide	7
346	Laundry	2066
349	Fiber	25
359	Insecticides	5
361	Metalware	15
366	Refractories	90
367	Magnesia products	2
370	Vitrified tile	25
371	Vitrified tile	19
372	Cleaning	9

The facilities offered by the Institute for systematic training in research methods have led to the establishment of another educational relationship—temporary assistantships, which are

available on Industrial Fellowships that will benefit thereby and whose donors approve. According to the usual arrangement, properly qualified engineering students of the university are placed in salaried assistantships during the periods when regular coöperative work is required. It carries the proviso that the student's thesis work is to be done under the direct supervision of the Industrial Fellow under whom the student has temporary employment. This system of temporary assistantships furnishes opportunities for the well-trained student to carry out technically important research and thus come under the observation of the executive staff.

During the Institute year the following students in the Department of Chemical Engineering held assistantships in the Institute:

D. E. Ackerman.....Nickel
C. D. Butterworth.....Nickel
W. C. Mellott.....Cleaning
W. M. Walker.....Refractories

PARIS LETTER

By Charles Lormand, 4 Avenue de l'Observatoire, Paris, France

Admission of Germany to International Union

The International Conference of Chemistry, which is to be held in June at Cambridge, will probably take up again, under a more or less disguised form, the question of admitting Germany to the International Union. It is not without interest to reflect a little on this question in order not to be taken unawares if an opinion is asked.

Prof. W. A. Noyes published in This Journal, in December, 1922, an article which is very interesting and which has been much commented upon in France. No one in France denies the place which Germany should be given in the International Union. She has many eminent chemists and we all know the world supremacy which her chemical industry formerly possessed. The necessities of war forced America, England, Italy, and France to create and develop their chemical industry. These nations showed that they too had the knowledge and ability to hold a place of the first rank in chemical research and its applications to industry. It is not, then, because they would need Germany's coöperation that they would admit her to the Union. As has been very well said by Professor Noyes, it is for the men of science to take the lead in bringing about a genuine and complete peace among the nations; it is certainly for the intellectual leaders to precede the politicians in the road to peace. Before agreement can be made as to the principles, a means of practical realization must be found.

The policy of the French government in matters of reparations obliged us to occupy the Ruhr. Whatever may have been the opinion as to the value of this policy and its consequences, it should be recognized that it receives general assent in France. Industrial leaders, and particularly those belonging to the chemical industry, favor this policy and in consequence sustain the government. The great majority of French chemists belong to various departments of the government; the universities are not independent as in the United States—the professors are all government officials, and they would not openly oppose the official policy. I know that there is objection to the opinion that the old university spirit has always maintained a stiff independence, and I do not forget that under the second empire the professors and republican thinkers (Quinet and Michelet) would not bother to oppose the imperial authority. But then it was a matter of national government, whereas we are now concerned with an international question where it is not asked that employees of the state take an attitude which would be interpreted as a repudiation of the acts of the government. All these obstacles, however, would be easily raised if the matter were placed on the sole ground of intellectual leaders establishing a true society of nations.

An organization filial to the Society of Nations has been functioning for more than three years with general satisfaction. This is the International Organization of Labor, whose bureau is located at Geneva, and which assembles at its conferences delegates of nations which were formerly allied or enemies. English, Belgians, Italians, French meet there with the Germans and the Austrians. The United States does not figure in this organization, although the questions of organization of labor are being studied there more than anywhere else. However, since January, it has consented to take part in the deliberations of a commission to consider the coal situation. This will perhaps lead to the United States taking a greater part in the International Organization of Labor. Here is, then, an organization, which, in France, meets an adhesion to principle, the practicality of which is not contested.

The International Union of Chemistry, even with the Germans, would meet the same unanimity, if the German intellectual leaders would previously admit their error. All the civilized nations have not forgotten the famous manifesto of the ninety-three German intellectual leaders, among which figured, unfortunately, several chemists and physicians. I do not remember the terms of that abominable factum, which dishonored the German intellectual leaders, but if those who signed it, and their successors, would consent to make a public disavowal of it, the question of the admission to Germany in the various international unions would make a great step toward being answered.

Use of Hot Springs as Source of Heat

It is well known that France possesses a certain number of hot springs, of which many have a temperature of more than 50° C. M. Dybowski has studied a spring at Prechacq, in the Pyrenees. This spring, which has a temperature of 60° C., delivers 50 cu. m. per hr., or a number of calories of heat equivalent to a ton of coal. M. Dybowski conceived the idea of using these calories and has had constructed heating chambers or "forceries," where on a large scale are cultivated certain fruits which can be gathered before their natural time, which are called in France "primeurs." These "forceries," much less cumbersome than those using coal, may be interesting to the United States in the Rocky Mountain region, at a sufficient distance from California and rich in hot springs.

Denaturant for Alcohol

The alcohols from the beet, grain, and molasses used by industry are denatured by methylene, but the entire market for methylene is now in the hands of England. In order to obtain the methylene which we need to denature our alcohol, we have to pay annually 22 million francs. In order to get rid of this expense, MM. Bordas and Touplain, of the Ministry of Finance, have undertaken the manufacture of a denaturant, called "denaturant national," with which the denaturing of our stock of alcohol will save us more than 125,000 francs. This denaturant is extracted from the oil from the distillation of resin, tars, and pitch, and the terebinth from pine. In it is incorporated an ester of boric acid which permits the easy detection of this denaturant.

Professor Urbain Visits America

Georges Urbain, member of the Institute, professor of general chemistry at the Faculté des Sciences de L'Université de Paris, has just departed for America. M. Urbain is a member of the International Committee on Atomic Weights, and it is well known that he is one of the leaders in mineral chemistry, particularly in the field of rare earths. To him we owe the discovery of the new elements europium and celtium.

March 29, 1923

Skinner, Sherman & Esselen, Inc., Boston, Mass., have moved their offices and laboratories to new and enlarged quarters at 276 Stuart St., Arlington, Mass. The change gives them an opportunity to lay out numerous laboratories for specific purposes, and their research, analytical, and biological departments now have quarters particularly designed for them and equipped in the most complete manner.

WASHINGTON NOTES

Research Council Elects Officers

The annual meeting of the Division of Chemistry and Chemical Technology of the National Research Council was held in the Sterling Chemistry Laboratory, Yale University, New Haven, Conn., on April 7. The following nominations for officers and members of the division for the year 1923–1924 were approved:

Chairman: J. E. Zanetti, Columbia University
Vice Chairman: J. F. Norris, Massachusetts Institute of Technology
Executive Committee:
E. W. Washburn, Editor, International Critical Tables
R. B. Moore, Bureau of Mines
L. W. Jones, Princeton University
Acheson Smith, Acheson Graphite Company
S. C. Lind, Bureau of Mines
Members of the Division:
Nominated by American Chemical Society:

E. C. Franklin	Wm. Hoskins	W. D. Bigelow
John Johnston	C. L. Parsons	H. P. Cady
J. E. Teeple	W. T. Taggart	F. J. Moore

Nominated by American Electrochemical Society: Acheson Smith
Nominated by American Institute of Chemical Engineers: C. L. Reese
Nominated by American Ceramic Society: A. V. Bleininger
Members-at-Large:

T. B. Johnson	W. C. Geer	S. C. Lind
R. B. Moore	L. W. Jones	H. N. Holmes

The main work of the division during the year was the organization of the work of International Critical Tables. The following projects were suggested for work during the ensuing year: (1) laboratory for thermochemical investigations; (2) a source of monochromatic ultra-violet light of great intensity; (3) the formulation of a list of research problems; (4) biochemical research; and (5) critical reviews on chemical topics. The following motions were adopted:

1—That the division recommend to the Executive Board of the Council the appointment of a small committee to discuss with Secretary Hoover and the Director of the Bureau of Standards the possibility of establishing such a thermochemical laboratory in the bureau, and ways and means by which the division and the chemists of the country might assist in the inauguration and systematic prosecution of a program of thermochemical investigation by the bureau.

2—That the division request Dr. Bancroft to prepare for publication a revised list of problems in colloid chemistry.

3—That the executive committee of the division be instructed to investigate the possibility of publishing critical reviews on chemical topics, and to secure, if possible, the coöperation of the American Chemical Society in establishing such a series to supplement its present Monograph Series.

Industrial-Alcohol Committee Appointed

Commissioner of Internal Revenue Blair has appointed the following advisory committee from the industry and consumers to consult on all matters affecting industrial alcohol:

H. E. Howe, Washington, D. C., Editor of *Industrial and Engineering Chemistry*, representing the American Chemical Society.
Wm. A. Sailer, Baltimore, Md., President of Sharpe and Dohme, and also President of the American Drug Manufacturers' Association.
W. J. Schieffelin, New York City, representing the National Wholesale Druggists' Association.
Samuel C. Henry, Chicago, Ill., representing the National Association of Retail Druggists.
J. H. Beal, University of Illinois, Urbana, Ill., representing the American Pharmaceutical Association and faculties of pharmaceutical colleges.
Martin Ittner, Chief Chemist, Colgate and Co., Jersey City, N. J., representing the American Manufacturers of Toilet Articles.
Frank A. Blair, New York City, President of the Proprietary Association.
M. C. Whitaker, New York City, President of the U. S. Industrial Chemical Co., Perkin Medalist, 1922.
R. H. Bond, Baltimore, Md., Manager of McCormick & Co., representing the Flavoring Extract Manufacturers' Association.
Charles L. Reese, Chief Chemist, E. I. du Pont de Nemours & Co., President of the Manufacturing Chemists' Association.

Bureau of Chemistry Conference

A general conference of the field force and staff assistants of the Bureau of Chemistry will be held in Washington during the week of May 21 to discuss and formulate plans for next year's work. About sixty out-of-town members of the bureau will attend this conference. This general conference will take the place of the district conferences which are usually held during April or May in New York, Chicago, or San Francisco.

Department of Public Works to Be Pushed by Engineers Committee

The Federated American Engineering Societies has appointed a national committee to aid President Harding in his plan for government reorganization. This committee is headed by J. Parke Channing, of New York, as chairman, and Philip N. Moore, of St. Louis, as vice chairman. The committee, which will be known officially as the Committee on Government Reorganization as It Relates to Engineering Matters, has been chosen with special care, and includes many of the best-trained minds on this subject.

Tariff Commission Extends Work

C. R. DeLong, chief chemist of the Tariff Commission, will sail for England on May 3, for the purpose of investigating the cost of production of oxalic acid, diethyl barbituric acid and derivatives thereof, barium dioxide, logwood extract, potassium chlorate, and sodium nitrite. He will be accompanied by M. G. Donk and E. M. Whitcomb, and will be gone about two months. His assistants, however, will remain abroad for a considerably longer time. F. W. McSparren and Edwin Schoenrich sailed for Argentina on April 14 on a similar mission with respect to casein.

Foreign Chemists Entertained

On Monday evening, April 16, a dinner was given at the Cosmos Club to Prince Gelasio Caetani and the following distinguished foreign chemists who came to America to attend the dedication of the Sterling Chemistry Laboratory during the recent meeting of the American Chemical Society at New Haven:

Frederick C. Donnan, Professor of Physical and Inorganic Chemistry, University College, London
Guiseppe Bruni, Director of Research, Pirelli & Co., Milan
James Colquhous Irvine, Principal and Vice Chancellor, University of St. Andrews
Arnold F. Holleman, Professor of Chemistry, University of Amsterdam

The others present were:

H. Foster Bain, Director, Bureau of Mines
E. D. Ball, Assistant Secretary of Agriculture
W. D. Bigelow, Chief Chemist, National Canners Association
William Mansfield Clark, Chief Chemist, Hygienic Laboratory
Wm. M. Corse, Director, Industrial Relations, National Research Council
F. C. Cottrell, Director, Fixed Nitrogen Laboratory
Charles R. DeLong, Chief Chemist, Tariff Commission
James N. Doran, Chief Chemist, Prohibition Unit Treasury Department
Richard Franchot
Amos A. Fries, Chief, Chemical Warfare Service
W. F. Hillebrand, Chief Chemist, Bureau of Standards
H. E. Howe, Editor, *Industrial and Engineering Chemistry*
Vernon Kellogg, Secretary, National Research Council
R. S. McBride, Assistant Editor, *Chemical and Metallurgical Engineering*
R. B. Moore, Chief Chemist, Bureau of Mines
Charles L. Parsons, Secretary, American Chemical Society
Atherton Seidell, Hygienic Laboratory
W. W. Skinner, Assistant Chief, Bureau of Chemistry
Edward E. Slosson, Director, Science Service
R. S. Sosman, Geophysical Laboratory
E. W. Washburn, Chief, Division of Chemistry and Chemical Technology, National Research Council
Percy Walker, Bureau of Standards
H. S. Washington, Geophysical Laboratory
T. S. Wilkinson, Ordnance Department, Navy Department

Dr. Parsons acted as toastmaster, and introduced the foreign guests, including the Italian Ambassador, all of whom spoke in a delightful manner and complimented America upon the part she has played in the advancement of chemistry.

On Tuesday evening, April 17, the Washington Academy of Science, the Philosophical Society of Washington, and the Chemical Society of Washington held a joint meeting in the auditorium of the Interior Building. The speakers of the evening were F. G. Donnan and James C. Irvine, who dedelivered masterly addresses on their recent researches in chemistry. Immediately preceding the meeting the speakers and two other distinguished foreign chemists, Guiseppe Bruni and A. G. Holleman, were the guests of the societies at a dinner at the Ebbitt Hotel.

April 18, 1923

BOOK REVIEWS

Glue and Gelatin. By JEROME ALEXANDER. American Chemical Society Monograph Series. 236 pp. The Chemical Catalog Co., Inc., New York, 1923. Price, $3.00.

Increasing interest in the chemistry of the proteins makes every serious contribution to the subject welcome. In the present volume a lively yet critical survey of part of this field is wedded to a careful and authoritative exposition of the manufacture and uses of the material discussed, so that the welcome is more than doubled.

The work fulfils in good measure the two chief purposes which the AMERICAN CHEMICAL SOCIETY has stated to be the object of these monographs: firstly, it gives an eminently readable account of "the knowledge available upon the chosen topic, intelligible to those not specialists in the subject;" secondly, it presents "a well-digested survey of progress already made," thereby promoting research in the subject. The readableness is perhaps enhanced by the absence of diagrams and illustrations in the text. The frontispiece illustrating the use of glue in Egypt, B. C. 1400, and the somewhat Goldbergian tailpiece showing a jelly tester, embrace a span devoid of either the picture that often spoils a story or the diagram that sometimes helps a theory. If this were the only book on the subject, one might quarrel with this restriction, but actually it helps the work's distinctive character.

Apart from the introduction, the book falls into two parts. Chapters 2 to 7 are primarily theoretical, and chiefly concerned with the conflicting views on proteins and colloids. Chapters 8 to 14 deal with the practical aspects of the technology and manufacture. In the former, the theme is keyed in a somewhat polemical mood, noticeably differing from the concise yet straightaway style of the latter portion. Here, without tinge of dogmatism, the author is speaking with authority from a long and intimate personal knowledge of the subject in all its details. There he is defending territory which was open range for loose but flexible colloid chemical conceptions, and attacking the construction gangs and homesteaders bent on threading it with curves and fencing it in with mathematical formulas. The attack on the "classical" physical chemistry view of proteins including gelatin, as variously pictured by Pauli, Procter, Wilson, Loeb and his collaborators, is better delivered than the presentation of the "colloid" or "dispersoid" countertheory. The author refers with approval to the idea of a progression of electronic→atomic→molecular→molar forces, according to which "each group of forces may be regarded as the residual fields remaining unsaturated in the smaller systems constituting the components of the system under consideration." This is plausible enough, but is it very useful? In the solid state par excellence, the crystalline in many cases, it appears that interatomic forces are operative directly, not "residual molecular" fields. The capitalization of nonspecific residual fields, even under the aegis of statistical mechanics, tends to yield ever-lessening dividends. The definite conceptions of Langmuir as to surface adsorption already show more solid gains than the empirical adsorption formulas. If the fixation of acids and bases by gelatin is to be ascribed to adsorption in the sense of Langmuir, it will not differ noticeably from chemical combination. At the same time, the author's criticism gives much food for thought and is definitely constructive. In dealing with the emulsoid colloids it is probable that the subdivision factor was overestimated as compared with reaction with the medium. On the other hand, the tendency lately has been to overemphasize this, and underestimate the importance of subdivision of phase. The insistence of Alexander on this factor, and on the complexity of the protein entity ("dissolecule," as contrasted with molecule, one is tempted to term it) is timely. There seems a tendency to assume that the primitive forms of the electrolytic-dissociation theory known to be inadequate for other than infinitely dilute crystalloid solutions are quite equal to the occasions of colloidal sols and gels. The author's warning (p. 59) against the use of pH units for scaling H-ion values is rather weakened than otherwise by the reference in the footnote to "erroneous curves of this character" used by Loeb. Such a scale is not itself erroneous, although it may be misleading.

Consistent with the author's viewpoint, the chapter on the structure of gelatin solutions and jellies is perhaps the most satisfactory in this part of the book, and strikes a very fair balance among the different hypotheses. The statement that Nägeli in 1858 "advanced the *micellular* theory, in which, etc.," seems questionable. The reviewer's understanding is that Nägeli meant by a micelle, not an "anisotropic crystal-like aggregate of molecules," but a crumb-like aggregation of crystallites—which is rather different. The spellings "micell" and "micellular" tend to suggest at least a philological connection with cells and the cell theory, whereas none was intended or sustained. The alternatives "micelle" and "micellar" seem less ambiguous. They are also consistent with the significance attached to the term by the French workers, as Duclaux, and by McBain in England. Turning to the more definitely technical part, the description of manufacturing methods is pithy yet informative. The discussions of the chemical examination, of physical testing, and of grading are full and valuable. The necessity of subordinating these to the economic law of supply and demand is emphasized early and late, and the critical importance of tests specific to the *use* of the material justly insisted upon. The utility of selected "standard glues" for rapid comparative testing is well brought out in this connection. At the same time, the reviewer would suggest that the physical tests of an "absolute" character, by which the "standards" themselves are judged invite drastic revision in the light of the advances in physical chemistry. "Finger tests" and "rule of thumb" will always have their place in the production of glue and gelatin, but their say in the matter should be for the day, and not for the year.

The book appears very free from typographic errors; the printing and set-up are clear and convenient. In these small details, as in its main matter and manner, it is to be cordially recommended.

S. E. SHEPPARD

Official Directory of Members of the Association of British Chemical Manufacturers with Classified List of Their Manufactures. 319 pp. The Association of British Chemical Manufacturers, Inc., 166, Piccadilly, London, W. 1, 1923. Price, 10s 6d.

This book contains a list of about 150 bona fide chemical manufacturers with a classified list of the products which they manufacture, and includes a section devoted to proprietary and trade names. The new list of products is given in considerably more detail than in the previous edition, and is translated into French, German, Italian, Spanish, and Portuguese. The object of the publication is to facilitate business relations between chemical manufacturers and purchasers all over the world.

The Analysis of Rubber. By JOHN B. TUTTLE. American Chemical Society Monograph Series. 155 pp. The Chemical Catalog Co., Inc., New York, 1922. Price, $2.50.

The chemist who is not familiar with the analysis of rubber goods will find this book of interest. It contains the usual methods for the determination of the acetone, chloroform, and alcoholic-potash extracts of rubber by the direct and indirect methods; of sulfur as it occurs in rubber goods, and of the various other ingredients used. In addition, the author has briefly described the various crude rubbers, the composition of crude rubber, the theory of vulcanization, and the ingredients used in the compounding of rubber.

The appendix is too brief. It contains a description of a few of the most common processes used in the manufacture of rubber goods and of the methods of determining their physical properties. A thorough knowledge of the manufacture and physical testing of rubber goods is essential to interpret properly the results of any analysis.

Chapter III contains a description of the various ingredients used in the compounding of rubber. The requirements and properties of many of these ingredients are given, together with the methods for their analysis. The rubber chemist will find this chapter of interest, for other authors have neglected to emphasize these points. However, this chapter would have been of great value if it had included all the properties of the ingredients and the methods for their analysis.

In Chapter IV the acetone extract is dried at 90° C. Most laboratories use 70° C.

Sodium hydroxide is not recommended for replacing potassium hydroxide in the preparation of alcoholic-potash solution. Some work at the Bureau of Standards showed that sodium hydroxide could be used to replace potassium hydroxide.

A mixture of ether and carbon tetrachloride is recommended instead of carbon tetrachloride in the determination of the waxy hydrocarbons.

The author states that the nitrosite method is the best for the determination of rubber. Unfortunately, the present data are limited to only a few compounds. The solution and ash methods are considered to be worthless. However, good results can be obtained by their use under proper conditions.

The determination of sulfur by the method of Kratz, Flower, and Coolidge is not mentioned. This method is used in many laboratories.

This book is too brief and it is hoped that a revised edition will soon follow.

S. COLLIER

Die Luftstickstoffindustrie, mit besonderer Berücksichtigung der Gewinnung von Ammoniak und Saltpetersäure. (The Nitrogen Fixation Industry, with Particular Reference to the Manufacture of Ammonia and Nitric Acid.) By DR. ING. BRUNO WAESER. viii + 586 pp. 72 figs. 25 × 17.5 cm. Otto Spamer, Leipzig, Täubchenweg 26, September, 1922. Price, unbound, 33,600 mk.; bound, 42,000 mk.

This volume is a handbook of the nitrogen-fixation industry and a digest of the technical literature of the various processes of nitrogen fixation.

The first 250 pages are devoted to a remarkably full statement of the development, the present status, and the economics of this industry. The chapter on the fixation industry in Germany occupies nearly 100 pages, and is particularly complete and illuminating. The remaining 350 pages of the book contain a careful digest of the literature bearing on the synthesis of ammonia by the cyanamide, nitride, and Haber-Bosch methods; and on the manufacture of nitric acid from saltpeter in the arc and by the catalytic oxidation of ammonia. Finally, there is an extensive tabular bibliography.

So far as the technical processes are concerned, there is little attempt at a critical treatment. The author appears to rely wholly on published material, and there are no disclosures, for instance, of the technical details of the Oppau and Leuna (Merseburg) Haber-Bosch plants. There are some surprising inequalities in the thoroughness of the treatment; the Bucher process is described in great detail and at great length, but there is no mention of the Mehner process. Similarly, the author appears never to have seen the uniquely valuable report of the British Munitions-Inventions Department, or the reports of our own War Department.

The treatment is concise, and the volume is printed in small type on a large page, so that the book is a veritable mine of information and statistics. It is, in fact, a monumental compendium, after the most approved Teutonic models. It should be of great value to the chemist, the economist, or the manufacturer interested in the history, the present status, and the future development of the fixed-nitrogen industry. Unfortunately, it only covers the period up to the spring of 1921, and in so rapidly developing an industry is, therefore, already somewhat out of date.

ARTHUR B. LAMB

Industrial Organic Chemistry. By SAMUEL P. SADTLER, PH.D., and LOUIS J. MATOS, PH.D. 5th edition, revised, enlarged, and in part rewritten. vi + 691 pp. J. B. Lippincott Co., Philadelphia and London. Price, $8.00.

The fourth edition of Dr. Sadtler's well-known book appeared in 1912. The growth of the organic chemical industries in the United States in the last ten years made it necessary to revise the text thoroughly. In order to do this the author associated with himself Dr. Matos, who has rewritten over one-third of the book. This material includes the chapters on textile fibers, coal-tar distillation and its products, dyes and bleaching, dyeing, and textile printing. The rest of the book has been revised by Dr. Sadtler, who has included accounts of the recent work on the utilization of cellulose, wood distillation, and the petroleum and oil-shale industries. Many improved analytical methods are described.

The book in its present form covers a very wide range of subjects, and the treatment of each one must of necessity be limited in scope. It is evidently designed more for the general reader than for the specialist in any particular field; and from this point of view it is to be highly commended. In general, the more important recent developments in the industries have been included. In certain cases, however, in the opinion of the reviewer, the treatment is inadequate. Very little space is given to one of the most important branches of the petroleum industry —namely, the cracking of oils and the utilization of the by-products formed.

The statements in regard to gasoline could be amplified. Here and there important advances have been overlooked. For example, in the paragraph on the use of chemicals foreign to bread in bread-making, reference is made to Liebig's suggestion of the use of limewater and the statement of Jago (1886) as to the benefit to be derived from this material. The large amount of work which has been done in this field at the Mellon Institute and elsewhere is not mentioned.

There are a few omissions from the index. For example, butyl alcohol, isopropyl alcohol, and propylene are described but do not appear in the index.

While the expert will find omissions here and there, it is important to emphasize the fact that the book covers the field adequately, and that this new edition makes it the best general treatment of the organic chemical industries that we have. It should be available to every student of organic chemistry.

JAMES F. NORRIS

Engine Room Chemistry. By A. H. Gill. 174 pp. McGraw-Hill Book Co., New York, 1922. Price, $2.00.

It is very difficult for a chemist to review properly a book which purports to be designed for the engineer or engine man in a power plant. What is good enough for the engineer may be elemental to the chemist, but, at the same time, in either case the material should be accurate and up to date. This volume purports to be a third edition, rewritten and brought thoroughly up to date.

We have before us the original edition, issued in 1907, and, with very few exceptions, the text is identical with what it was fifteen or sixteen years ago. The old references given at that time continue in the present issue. The material at that time was valuable, but some of it at the present time is not as thoroughly up to date as it might be.

A careful comparison of this volume with the first edition shows that the Thompson, the Barrus, as well as the old Parr calorimeter, are still illustrated and carefully described, while only reference is made to the new Parr and the Mahler bomb type of calorimeter. Many of the instruments described would be found to-day only in a curio shop.

Methods of coal analysis refer back to 1899, whereas the standard methods developed by the A. S. T. M. have been ignored. Some space is consumed in telling how heat value can be calculated from ultimate analysis, although the determination of the heat value would cost approximately one-tenth that of the ultimate analysis.

Some errors in the first edition are still carried on in this third edition—as, for instance, on page 23 a 10 per cent solution of the salt is described as 2.5 g. to 250 cc. of distilled water.

On page 50, a table mixes together Baumé and specific gravity in one column.

Some new material appears relative to combustion and the calculation of combustion tests. In fact, most of the new material occurs in the chapter on combustion.

In the chapter on water, "soda crystals" with 10 H_2O are referred to frequently, whereas at the present time soda ash is the only form in which carbonate of soda is generally used. The old tabulation of heat losses through scale thicknesses, which has appeared since Kent's first volume, and which has never been supported by facts, is still included, and when characteristic analyses are printed they are usually English analyses taken from some obsolete text.

In the chapter on oils no reference is made to southern or western oils, Pennsylvania and Ohio being the only states in the United States from which petroleum is apparently obtained. On page 110, where tests on lubricating oils are shown, viscosity figures based upon obsolete instruments are included, where it would have been much better to have given a new tabulation of results on the Saybolt Universal, which is referred to later in the chapter. Space is wasted in describing the old Saybolt equipment, now practically out of use. Where the "pour" test is generally used, a "cold" test is described, and where a flash thermometer standardized to 1-in. immersion is used, $^1/_2$-in. immersion is the description in the text. Other tests are given which have little standing, and the values of the carbon test and the emulsion test are overlooked completely.

On page 146, however, where up-to-date specifications are tabulated, the carbon residue and the "pour" test specifications are shown with absolutely no explanatory material in the text.

If we are to assume the engineer to be ignorant, for whom anything is good enough, this volume, no doubt, will be suitable, but, with the engineer progressing as rapidly as he is at the present time, we would consider this text a little old-fashioned and considerably out of date in a great many respects.

D. K. French

The Nitrogen Industry. By J. R. Partington, M.B.E., D.Sc., and L. H. Parker, M.A., D.Sc., F.I.C. 336 pp. D. Van Nostrand Co., New York, 1923. Price, $6.00.

This is a readable, not very technical account of the nitrogen industry, which might have considerable value in orienting persons contemplating engaging in some branch of the nitrogen industry. The book contains many pleas for an increased development of nitrogen fixation in England from the point of view of national preparedness, and criticizes the British government for its handling of the situation.

The authors describe the Chile nitrate industry, the production of by-product ammonia and ammonium sulfate, the fixation of nitrogen by the synthetic ammonia, cyanamide, and arc processes, and the oxidation of ammonia.

The economic side of the problems of the nitrogen industry is quite completely handled, largely by means of tables taken from the "Final Report of the Nitrogen Products Committee" of the British government.

The book contains but little material of interest to chemists or chemical engineers who have actually got to the stage of developing nitrogen-fixation processes. Thus, there is no treatment of catalysts for the synthetic-ammonia process, no discussion of the rates of reaction which determine the yield of the arc process, and, in general, no fundamental discussion of the chemistry of any of the processes.

There are a number of incorrect statements concerning the progress of nitrogen fixation in America, and the book was apparently completed before the publication by our own Government of the "Report on the Fixation and Utilization of Nitrogen."[1] This latter report combined with the British report mentioned above contains on the whole a much more satisfactory and complete account of the nitrogen industry than the book, except for the interesting treatment of the Chile nitrate industry which the book contains and which is not readily available elsewhere.

Richard C. Tolman

[1] Government Printing Office, No. 2041.

The Bureau of Mines, Its History, Activities, and Organization. By Fred W. Powell. Service Monographs of the United States Government, No. 3. 162 pp. Institute for Government Research, Washington. Price, $1.00.

This monograph is the third in a series compiled and published by the Institute for Government Research for the purpose of "furnishing an essential tool for efficient legislation, administration, and popular control, and of laying the basis for critical and constructive work on the part of those upon whom responsibility for such work primarily rests."

In common with other numbers of this monograph series, this discussion of the Bureau of Mines is very complete, embracing the history of the bureau, its activities, its organization in considerable detail, the character of its equipment, a compilation of the laws and regulations governing its operations, financial statements showing appropriations and expenditures, and a bibliography indicating the sources from which the information presented in the monograph has been drawn.

The activities are discussed under the principal headings of promotion of safety and health, investigation of mine hazards, technological research and investigations, the administration duties of the bureau, the war activities, and the compilation of mining laws and regulations.

The monograph will be very useful to all those interested in the work of the Bureau of Mines and to any who may have before them the task of creating an organization to deal with a project of similar magnitude and complexity. It will give to the public a knowledge of the organization and operation of the bureau which will enable it to give its work further support.

COMMERCE REPORTS

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.*

March

The total production of **petroleum** in Russia during the twelve months ended September 30, 1922, showed an increase of about 20 per cent as compared with the preceding twelve months. (P. 613)

The discovery of a new fiber, **malvavisco**, which is said to be a substitute for jute, is announced by the Industrial Experiment Laboratory of the Mexican Department of Commerce and Industry. Prolonged experiments have shown this plant to possess qualities similar to jute and the cost of extracting the fiber to be small. (P. 615)

The Mexican market for **drugs** and **chemicals** is reviewed. At the present time the United States supplies about 60 per cent of Mexico's import trade in these products. (Pp. 617–8)

A firm in Sweden has recently offered large quantities of **perchlorate of ammonium** for sale. Further information may be obtained from the Chemical Division of the Bureau of Foreign and Domestic Commerce. (P. 619)

The German production of **lignite** is increasing, but only a small portion, about 2 per cent, is used as a raw material in the manufacture of chemicals. (P. 620)

A German architect is said to have invented a successful process for the manufacture of furniture from **pulp**. The product is said to be durable and less expensive than wooden furniture. (P. 626)

The Commonwealth of Australia has revoked the order issued on December 2, 1920, which restricted the importation of **carbide of calcium**. (P. 636)

The duty on **fusel oil** exported from Rumania has been fixed at 2.30 lei per kilo. (P. 638)

The value of the **mineral output** of British Columbia for the year 1922 has been estimated by the Minister of Mines at $32,167,463, as compared with $28,066,641 for the previous year. The production of silver was the highest in the history of the Province, being 25 per cent greater than in 1897, the previous record year. (P. 674)

There is a growing demand for **artificial leather** in British South Africa. (P. 678)

The long-debated bill designed to bring about certain reforms in the Columbian **oil laws** was passed by the Columbian Congress shortly before its adjournment on January 26. (P. 689)

A new set of regulations governing the exportation and local sale of refining of Rumanian **petroleum products** have been published and copies of the schedules contained in the regulations will be made available to interested parties by the Petroleum Division of the Bureau of Foreign and Domestic Commerce. (P. 689)

The manufacture of **artificial ice** is one of the minor industries of Boulogne-sur-Mer. American ammonia was formerly used but high exchange has caused it to be replaced by synthetic ammonia of French manufacture. (P. 693)

Imports into the United States for the eleven months from January 1 to November 30, 1922, of **chemicals and allied products** (excluding gums, resins, and crude oils) had an aggregate value of $93,070,171—an increase of 24 per cent over the corresponding period of 1921, whereas the value of domestic exports for the same months showed an increase of but 1 per cent over the preceding year. (Pp. 734–5)

The French **chemical market** is active and the market for certain specified chemicals is described. (P. 735)

Japan's **caustic soda** trade is reviewed. (P. 736)

The United States increased its purchases of foreign **vegetable dye extracts, coloring material**, etc., more than 300 per cent in quantity and 200 per cent in value during the eleven months of 1922 as compared with the previous year. Of the 1922 imports, 655,559 lbs., valued at $40,019, were received after September 22. (P. 736)

Rather authentic estimates place the average daily production of **artificial silk** in England and on the Continent at the following figures: England, 15,000 lbs.; France, 30,000 lbs.; Germany, 35,000 lbs.; Switzerland, 20,000 lbs.; Netherlands, 4000 lbs.; Italy, 20,000 lbs.; Japan, 2000 lbs.; Poland, 2000 lbs.; Belgium, 25,000 lbs. (P. 739)

The quantity of **petroleum products** sold in Belgium in 1922 was much greater than during 1921. Large quantities of gasoline and kerosene were bought for future use on account of the low prices. Lubricating oil was consumed to a greater extent than in 1921, as was also fuel oil for industrial purposes. (P. 752)

The **shale oil** operations of John Fell & Co., at Newnes, New South Wales, have been discontinued owing to the high cost of production. (P. 753)

According to a recent decree of San Salvador, **pharmaceutical specialties** with a base of chemically pure paraffin oil are hereafter to be dutiable at 40 cents gold per kilo, instead of $1.00 per kilo, the rate formerly assigned to pharmaceutical specialties imported in liquid form and not regarded as consumer's goods. (P. 768)

With but two exceptions, nickel oxide and nitrate of soda, imports into the United Kingdom of all **chemical manufactures** (other than drugs and medicines) named in the official returns of British trade were higher in quantity in 1922 than in the preceding year. In average import price, the trend was downward, with acetic acid as an exception. (Pp. 797–9)

The commissioner appointed by the Danish government to investigate the possibility of manufacturing **nitrogen** in Denmark has made his report and states, as the results of his investigations, that Denmark is in position to produce its own nitrogen, and at competitive figures. In this connection it is interesting to note that before the war Danish consumption of Chilean saltpeter was 50,000 tons. (P. 799)

A Swedish sawmill operator recently laid particular stress upon the utilization of wood waste, especially the fact that his plant was generated by **gas** obtained from **wood waste**. In this manner the mill was able to save 75 per cent of the fuel ordinarily used when the sawdust and chips were fed directly under the boiler. Besides this saving in waste the company obtained valuable by-products, such as acids, wood alcohol, tar, etc. (Pp. 813–4)

The **vegetable-oil industry** of Hull, England, is reviewed. (Pp. 815–6)

The Danish **vegetable oil** and **oilseed trade** is described. (Pp. 816–7)

The year 1922 proved very unfavorable to the **petroleum trade** of Czechoslovakia. (P. 819)

The exportation of **copper, brass, nickel, cadmium, argentin, Brittania metal, lead shaving, filings,** and **lumps** from Poland is prohibited until further notice. (P. 829)

The importation, manufacture, transportation, holding, and sale of **saccharin** and similar products, or the importation and manufacture of products containing these substances, is prohibited in Belgium. (P. 829)

Statistics of Exports to the United States

Shanghai—(P. 640)
Antimony
Norway—(P. 675)
Aluminium
Australia—(P. 675)
Copper
Brazil—(P. 685)
Rubber
Aden—(P. 735)
Gum myrrh
Latvia—(P. 774)
Santonin
Platinum
Jugoslavia—(P. 775)
Cellulose
Egypt—(P. 836)
Gum arabic
Iron ore

CURRENT PUBLICATIONS

NEW BOOKS

American Society for Testing Materials: Index to Volumes XIII to XX (1913–1920). 189 pp. Price, $2.50. American Society for Testing Materials, Philadelphia.

Chemical Industry: Betriebsverrechnung in der chemischen Grossindustrie. ALBERT HEMPELMANN. 107 pp. Price, $1.40. Julius Springer, Berlin.

Chemical Industry: Taschenbuch für den Chemikalienhandel. J. BISCHOFF. 2nd edition. 334 pp. Price, $4.00. A. Ziemsen, Wittenberg.

Chemical Technology: Lehrbuch der Chemischen Technologie. H. OST. 13th edition. 815 pp. Price, 19s. Max Janecke, Leipzig.

Chemistry Tangle Unravelled. F. W. GRAY. 148 pp. Price, 6s. Longmans, Green & Co., London.

Cold: The Generation and Utilization of Cold: A General Discussion. THE FARADAY SOCIETY. 136 pp. Price, 10s. 6d. The Faraday Society, London.

Destructive Distillation of Wood. H. M. BUNBURY. 320 pp. Price, 35s. Benn Bros., Ltd., London.

Dictionary: Dizionario di Merceologia e di Chimica Applicata. Vol. I. Abelmosco-Cuscuta. G. VITTORIO VILLAVECCHIA. 4th edition. 871 pp. Price, 35 l. Ulrico Hoepli, Milan, Italy.

Drugs: Origin and History of All the Pharmacopeial Vegetable Drugs, Chemicals, and Preparations. Vol. I. Vegetable Drugs. JOHN URI LLOYD. 449 pp. Illustrated. Price, $6.00. American Drug Manufacturers' Assoc., Washington, D. C.

Dyes: Der Praktische Kleiderfärber. KARL BLAU. 345 pp. Price, $4.00. A. Ziemsen, Wittenberg.

Dyes and Their Application to Textile Fabrics. A. J. HALL. Pitman's Common Commodities and Industries. 116 pp. Price, 3s. Sir Isaac Pitman & Sons, Ltd., London.

Electrolytic Dissociation Theory with Some of Its Applications. An Elementary Treatise for the Use of Students of Chemistry. HENRY P. TALBOT AND ARTHUR A. BLANCHARD. 2nd edition. 85 pp. Price, $2.00. The Macmillan Co., New York.

Elementary Organic Chemistry. W. H. BARRETT. 256 pp. Price, $1.50. Oxford University Press, New York.

German Gun Steels. R. D. Report No. 57. RESEARCH DEPARTMENT, WOOLWICH. 16 pp. Price, 3s. H. M. Stationery Office, London.

Ink: Manuel Pratique de la Fabrication des Encres. L. DESMAREST AND S. LEHNER. Bibliotèque des Actualités Industrielles. No. 65. 3rd edition, revised and enlarged. 372 pp. Price, 12 fr. Gauthier-Villars & Cie., Paris.

Laboratory Organization: A Tested Method of Laboratory Organization. SEYMOUR PILE AND REGINALD G. JOHNSTON. 98 pp. Price, 7s. 6d. H. F. & G. Witherby, London.

Molybdenum (1913–1919). The Mineral Industry of the British Empire and Foreign Countries. IMPERIAL MINERAL RESOURCES BUREAU. 87 pp. Price, 1s. 6d. H. M. Stationery Office, London.

Organic Synthesis. Vol. II. J. BRYANT CONANT, Editor-in-chief. 100 pp. Price, 7s. 6d. Chapman & Hall, Ltd., London.

Patents—Law and Practice. Trade-Marks—Trade Names, Unfair Competition. 56 and 46 pp. Richards & Geier, New York.

Petrology. Vol. II. The Petrology of the Sedimentary Rocks. A Description of the Sediments and Their Metamorphic Derivatives. F. H. HATCH AND R. H. RASTALL. New edition. 368 pp. Price, $3.50. The Macmillan Co., New York.

Pottery: Die Tonwarenerzeugung. WILHELM RUDOLPH. 2nd edition, revised. 210 pp. Price, 4s. 3d. Max Zanecke, Leipzig.

Relativity: The Mathematical Theory of Relativity. A. S. EDDINGTON. 247 pp. Price, $6.75. The Macmillan Co., New York.

Riddle of the Rhine. VICTOR LEFEBURE. American edition. 282 pp. Price, $2.00. E. P. Dutton & Co., New York.

Silver (1913–1919). The Mineral Industry of the British Empire and Foreign Countries. IMPERIAL MINERAL RESOURCES BUREAU. 218 pp. Price, 4s. H. M. Stationery Office, London.

Solution: The Problem of Solution. STEPHEN MIALL. 33 pp. Price, 2s. Benn Bros., Ltd., London.

Strontium Minerals (1913–1919). The Mineral Industry of the British Empire and Foreign Countries. IMPERIAL MINERAL RESOURCES BUREAU. 12 pp. Price, 3d. H. M. Stationery Office, London.

Synthetic Coloring Matters: Vat Colors. J. F. THORPE AND C. K. INGOLD. Monographs on Industrial Chemistry. 491 pp. Price, $5.50 net. Longmans, Green & Co., New York.

Thermodynamics and the Free Energy of Chemical Substances. GILBERT N. LEWIS AND MERLE RANDALL. 658 pp. Price, $5.00. McGraw-Hill Book Co., Inc., New York.

Vegetable Fibers: Das Bleichender Pflanzenfäsern. W. KIND. 2nd edition. 375 pp. Price, $4.00. A Ziemsen, Wittenberg.

X-Rays. G. W. C. KAYE. 4th edition. 320 pp. Price, 16s. Longmans, Green & Co., London.

RECENT JOURNAL ARTICLES

Abrasives and Polishing Powders for Glass. JAMES WEIR FRENCH. *The Glass Industry*, Vol. 4 (1923), No. 4, pp. 65–68.

Aluminium: Influenza del Fosforo sulle Leghe d'Alluminio. LUIGI LOSANA. *Giornale di Chimica Industriale ed Applicata*, Vol. 5 (1923), No. 2, pp. 67–70.

Bromine: L'Industrie du Brome en Allemagne. M. DEBUSSY. *Chimie et industrie*, Vol. 9 (1923), No. 2, pp. 245–58.

Burning Blast Furnace Gas. GRANT D. BRADSHAW. *Blast Furnace and Steel Plant*, Vol. 11 (1923), No. 4. pp. 250–52.

Cellulose: The Effect of Hypochlorous Acid Solutions and of Bleaching Liquors on Cellulose. E. KNECHT AND J. P. EGAN. *Journal of the Society of Dyers and Colourists*, Vol. 39 (1923), No. 3, pp. 67–73.

Colloid Chemistry and Its Application in Pharmacy. C. B. JORDAN. *Journal of the American Pharmaceutical Association*, Vol. 12 (1923), No. 3, pp. 234–39.

Dyeing: Modern Equipment for Dyeing, Bleaching, and Finishing Operations. E. A. TURNER. *Canadian Colorist and Textile Processor*, Vol. 3 (1923), No. 3, pp. 4–10.

Feldspar: The Marketing of Feldspar. ARTHUR S. WATTS. *Engineering and Mining Journal-Press*, Vol. 115 (1923), No. 12, pp. 535–38.

Fuel: Selection of Fuel for Industrial Heating Operations. JOS. A. DOYLE. *Forging and Heat Treating*, Vol. 9 (1923), No. 3, pp. 156–60.

Glass: The Electrodeposition of Silver and Copper on Glass. CHARLES H. PROCTOR. *The Glass Industry*, Vol. 4 (1923), No. 4, pp. 61–63.

Glass: Étude Comparative des Verres de Laboratoire Préparés en France, en Angleterre, en Allemagne, et en Autriche. P. NICOLARDOT. *Chimie et industrie*, Vol. 9 (1923), No. 2, pp. 233–44.

Glass: Tests on the Resistive Qualities of Soda-Lime Glasses to Water. L. A. PALMER. *Journal of the American Ceramic Society*, Vol. 6 (1923), No. 4, pp. 579–88.

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Iron: Advantages of Basic-Electric-Furnace Iron for Castings to Resist Abrasion. LARRY J. BARTON. *Engineering and Mining Journal-Press*, Vol. 115 (1923), No. 14, pp. 628–30.

Leather: Sur la Neutralisation du Cuir au Chrome. LOUIS MEUNIER AND PAUL CHAMBARD. *Journal of the Society of Leather Trades' Chemists*, Vol. 7 (1923), No. 2, pp. 75–83.

Light and Color Phenomena. WEBSTER A. MELCHER. *Textile Colorist*, Vol. 45 (1923), No. 532, pp. 219–22.

Lime and Cotton. WILLIAM B. NANSON. *American Dyestuff Reporter*, Vol. 12 (1923), No. 7, pp. 241–46, 251–53.

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Paper: La Coloration du Papier. ANDRÉ BELTZER. *L'Industrie Chimique*, Vol. 10 (1923), No. 110, pp. 106–9.

Petroleum: Further Investigations into the Physicochemical Significance of Flash-Point Temperatures. W. R. ORMANDY AND E. C. CRAVEN. *Journal of the Institution of Petroleum Technologists*, Vol. 9 (1923), No. 35, pp. 33–60.

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Refractories: Metallurgical Requirements of Refractories for Furnaces Melting Copper Alloys. H. W. GILLETT. *Journal of the American Ceramic Society*, Vol. 6 (1923), No. 4, pp. 596–609.

Solvents: Study of the Solvents of Some Cellulose Esters. ERNEST WALTER AND JOHN MARDLES. *Journal of the Society of Chemical Industry*, Vol. 42 (1923), No. 13, pp. 126*t*–36*t*.

Rubber: Variability of Rubber. Effect of Organic Accelerators. G. MARTIN AND W. S. DAVEY. *Journal of the Society of Chemical Industry*, Vol. 42 (1923), No. 11, pp. 98*t*–106*t*.

Structural Colors in Feathers. I. CLYDE W. MASON. *Journal of Physical Chemistry*, Vol. 27 (1923), No. 3, pp. 201–51.

MANUFACTURERS' TECHNICAL PUBLICATIONS

Concrete: Integral Waterproofing: A Practical Discussion. SAMUEL R. T. VERY. An 8-page pamphlet reprinted from *Architecture*, dealing with this problem on the basis of an architect's investigations. TRUSCON LABORATORIES, Detroit, Mich.

Electric Motors: The Watson Multi-Speed. A 12-page pamphlet describing an alternating current motor with four or less synchronous speeds. LOUIS ALLIS CO., Milwaukee, Wis.

GOVERNMENT PUBLICATIONS

Notice—*Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate.*

Bureau of Mines

A Simple Method for the Determination of Tin in Iron and Steel. E. P. BARRETT AND J. D. SULLIVAN. *Reports of Investigations* 2459. 4 pp. Issued March, 1923.

Abstracts from the Literature on Treatment of Manganese Silver Ores. G. H. CLEVENGER AND ALPHONSO CORNEJO. *Reports of Investigations* 2458. 14 pp. Issued March, 1923.

Coal-Mine Fatalities in February, 1923. W. W. ADAMS. *Reports of Investigations* 2460. 3 pp. Issued March, 1923.

Effects of Temperature and Time of Reaction in Distilling Oil Shales on the Yields and Properties of the Crude Oils. L. C. KARRICK. *Reports of Investigations* 2456. 8 pp. Issued March, 1923.

Explosives Used in January, 1923. W. W. ADAMS. *Reports of Investigations* 2461. 4 pp. Issued March, 1923.

How Steam-Production Costs Were Reduced in a Hand-Fired Return Tubular Boiler Plant. A. R. MUMFORD. *Reports of Investigations* 2455. 14 pp. Issued March, 1923.

Metal-Mine Fires. DANIEL HARRINGTON, B. O. PICKARD, AND H. M. WOLFLIN. *Technical Paper* 314. 20 pp. Paper, 10 cents.

Production of Explosives in the United States during the Calendar Year 1921, with Notes on Mine Accidents Due to Explosives. W. W. ADAMS. *Technical Paper* 313. 25 pp. Paper, 5 cents.

Talc and Soapstone: Their Mining, Milling, Products, and Uses. R. B. LADOO. *Bulletin* 213. 133 pp. Paper, 25 cents.

The Chloride-Volatilization Process of Ore Treatment. THOMAS VARLEY, E. P. BARRETT, C. C. STEVENSON, AND R. H. BRADFORD. With an Introductory Chapter by STUART CROASDALE. *Bulletin* 211. 99 pp. Paper, 20 cents.

Transportation Systems at Lime-Plant Quarries. OLIVER BOWLES. *Reports of Investigations* 2454. 6 pp. Issued March, 1923.

Bureau of Standards

Composition, Purification, and Certain Constants of Ammonia. E. C. MCKELVY AND C. S. TAYLOR. *Scientific Paper* 465. Paper, 10 cents.

Lathe Breakdown Tests of Some Modern High-Speed Tool Steels. H. J. FRENCH AND JEROME STRAUSS. *Technologic Paper* 228. 43 pp. Issued February 17, 1923. Paper, 15 cents.

Shellac. P. H. WALKER AND L. L. STEELE. *Technologic Paper* 232. Paper, 5 cents.

Solder for Aluminium. *Circular* 78. Paper, 5 cents.

Specific Volume of Saturated Ammonia Vapor. C. S. CRAGOE, E. C. MCKELVY, AND G. F. O'CONNOR. *Scientific Paper* 467. Paper, 5 cents.

Tentative Standard Test Methods and Percentages of Oil and Moisture in Hair Press Cloths. F. R. MCGOWAN AND C. W. SCHOFFSTALL. *Technologic Paper* 231. 20 pp. Issued March 10, 1923. Paper, 5 cents.

United States Government Specification for Volatile Mineral Spirits for Thinning Paints. Federal Specifications Board. Standard Specification No. 16. *Circular* 98. 10 pp. Paper, 5 cents.

Bureau of the Census

Mines and Quarries, 1919. General Report and Analytical Tables and Reports for States and Selected Industries. 14th Census of the United States, 1920. Prepared under the supervision of E. F. HARTLEY by F. J. KATZ. 443 pp. Cloth, $1.25.

Congress

Narcotic Drugs. Joint Resolution requesting the President to urge upon the governments of certain nations the immediate necessity of limiting the production of habit-forming narcotic drugs and the raw materials from which they are made to the amount actually required for strictly medicinal and scientific purposes.

H. J. Res. 453. Introduced by MR. PORTER, February 17, 1923, referred to the Committee on Foreign Affairs and ordered to be printed; February 21, 1923, reported with amendments, referred to the House Calendar, and ordered to be printed. 6 pp.

S. Cal. 1228. February 26, 1923, read twice and referred to the Committee on Foreign Relations; February 26, reported by MR. LODGE without amendment. 6 pp.

Narcotic Drugs. Limiting the Production of Habit-Forming Narcotic Drugs and the Raw Materials from Which They Are Made.

H. Rep. 1678. Submitted by MR. PORTER, February 21, 1923. 7 pp.

S. Rep. 1234. Submitted by MR. LODGE, February 26, 1923. 7 pp.

National Hydraulic Laboratory. Hearing before a Subcommittee of the Committee on Commerce, United States Senate, pursuant to *S. J. Res.* 209 to establish a National Hydraulic Laboratory. September 8, 1922. 60 pp.

Naval Stores. *H. Rep.* 1655 to accompany H. Rep. 14,326. February 19, 1923, committed to the Committee of the Whole House on the state of the Union and ordered to be printed. 4 pp.

Nitrate of Soda and Calcium Arsenate:

Hearings on *S. J. Res.* 265, to stimulate crop production in the United States by the purchase of nitrate of soda and calcium arsenate and the disposal of same at cost. January 16 to February 2, 1923. 124 pp.

Joint Resolution to stimulate crop production in the United States. Union Calendar No. 557, *S. J. Res.* 265. January 16, 1923, referred to the Committee on Agriculture; February 5, 1923, reported with amendments, committed to the Committee of the Whole House on the state of the Union, and ordered to be printed. 2 pp.

Oil Pollution of Coastal Navigable Waters. *H. Rep.* 1693 to accompany S. 3968. Submitted by MR. DEMPSEY, February 23, 1923, referred to the House Calendar and ordered to be printed. 9 pp.

Department of Agriculture

Commercial Bordeaux Mixtures. How to Calculate Their Values. ERRETT WALLACE AND L. H. EVANS. *Farmers' Bulletin* 994. 11 pp.

Composition of Filter-Press (Lime) Cake. S. F. SHERWOOD. *Department Circular* 257. 3 pp. Paper, 5 cents.

The Influence of Copper Sprays on the Yield and Composition of the Irish Potato Tuber. F. C. COOK. *Department Bulletin* 1146. 26 pp. Issued April 5, 1923. Paper, 5 cents.

Turpentine and Rosin. V. E. GROTLISCH. *Department Circular* 258. 15 pp.

Vitamin B in the Edible Tissues of the Ox, Sheep, and Hog. I. Vitamin B in the Voluntary Muscle. II. Vitamin B in the Edible Viscera. RALPH HOAGLAND. *Department Bulletin* 1138. 48 pp. Paper, 10 cents.

Geological Survey

Economic Geology of the Summerfield and Woodsfield Quadrangles, Ohio. With Descriptions of Coal and Other Mineral Resources except Oil and Gas. D. D. CONDIT. *Bulletin* 720. 156 pp. Paper, 30 cents.

Gold, Silver, Copper, Lead, and Zinc in Colorado in 1921. Mines Report. C. W. HENDERSON. Separate from Mineral Resources of the United States, 1921, Part I. 33 pp. Published March 16, 1923.

Gold, Silver, Copper, Lead, and Zinc in New Mexico and Texas in 1921. Mines Report. C. W. HENDERSON. Separate from Mineral Resources of the United States, 1921, Part I. 11 pp. Published March 15, 1923.

Manganese Deposits of East Tennessee. G. W. STOSE AND F. C. SCHRADER. Prepared in Coöperation with the Tennessee State Geological Survey. *Bulletin* 737. 154 pp. Paper, 50 cents.

Surface Water Supply of the United States, 1918. Part X. The Great Basin. Prepared in Coöperation with the States of Utah, Nevada, California, Oregon, and Wyoming. N. C. GROVER, C. C. JACOB, A. B. PURTON, H. D. MCGLASHAN, F. F. HENSHAW, G. C. BALDWIN, AND ROBERT FOLLANSBEE. *Water-Supply Paper* 480. 271 pp. Paper, 20 cents.

Public Health Service

A Preliminary Report on the Use of Creosote Oil as a Mosquito Repellent. C. P. COOGLE. *Public Health Reports* 38 (March 9, 1923), 437–43.

Studies on Oxidation-Reduction. I. Introduction. W. M. CLARK. *Public Health Reports* 38 (March 16, 1923), 443–55.

Studies on the Bio-Assay of Pituitary Extracts. Concerning the Use of a Desiccated Infundibular Powder as a Standard in the Physiological Evaluation of Pituitary Extracts. M. I. SMITH AND W. T. MCCLOSKY. *Public Health Reports* 38 (March 16, 1923), 493–512.

Use of Liquid Eggs Found to Be Source of Boric Acid in Cake. *Public Health Reports* 38 (March 16, 1923), 512–3.

The Epidemiology of Botulism. J. C. GEIGER, E. C. DICKSON, AND K. F. MEYER. Prepared by Direction of the Surgeon General. *Public Health Bulletin* 127. 119 pp. Paper, 15 cents.

United States National Museum

On Siderite and Associated Minerals from the Columbia River Basalt at Spokane, Washington. E. V. SHANNON. No. 2458 from the Proceedings of the United States National Museum, Vol. 62, Art. 12, pp. 1–19.

MARKET REPORT—APRIL, 1923

[Supplied by Drug & Chemical Markets]

While business in the spot market has been quiet and spasmodic, manufacturers continue to report a steady demand for all kinds of chemicals. Industry throughout the country has been increasing steadily and consumption of chemicals has been keeping pace with the general expansion of business. The widespread boom in the building industry is consuming enormous quantities of metal and metal products. Pigments, paints, and varnishes are moving in the largest volume since the post-war boom. The automobile industry is consuming large quantities of chemical products. With the approach of spring demand for fertilizers and insecticides is coming from agricultural sections. Textile manufacturers are working on a full-time basis and the demand for textile chemicals and dyestuffs has increased. Most of these industries are receiving their requirements on contract and withdrawals have been increasing steadily. Transportation has improved throughout the country and consumers are having less difficulty in obtaining their supplies.

Outside of contract business, buying from spot stocks for speculation or resale to consumers has fallen off materially during the past month. Whether or not this has been induced by the generally higher levels which prices have reached, or whether it is the usual spring reaction that frequently follows heavy winter buying, it is impossible to determine at this time. Economists who have been predicting dire things if prices rose too rapidly are pointing to the lull and labeling it the product of higher prices. This condition is belied, however, by the fact that consuming industries are running full time and using more chemicals than ever, but to a great extent goods supplied on contract at prices well below the open market figures now ruling.

Each week imported chemicals play less and less an important role in the American markets. Shipments are still coming through from abroad in large lots, it is true, but the low prices abroad which held American production of chemicals at a minimum for three years, have now risen to a point where there is little choice in the matter of price as to whether the importer or American maker gets the order. Of course, the tariff is functioning and has done much to equalize the difference in costs, although the way in which the duties are working out in several cases has proved unsatisfactory. Many products are still insufficiently protected to compete with foreign goods, while instances where the duties are too high still continue to disturb the market.

Sulfuric acid and caustic soda are in great demand, and prices of the former have gradually stiffened and advanced to slightly higher level. Exports of caustic soda have been increasing, most of the shipments being consigned to Japan. Bleaching powder and chlorine are in active demand. Makers of Glauber's salts are unable to accumulate any surplus for the summer months. Copper sulfate has been moving slowly. Domestic production of caustic potash has been gaining steadily since the imported material has become scarce and higher in price. Ammonium sulfate continues scarce and in active demand. Sodium hyposulfite is lower. Copper oxide and carbonate are in good demand and prices firm. Tin compounds have advanced on higher costs of metal.

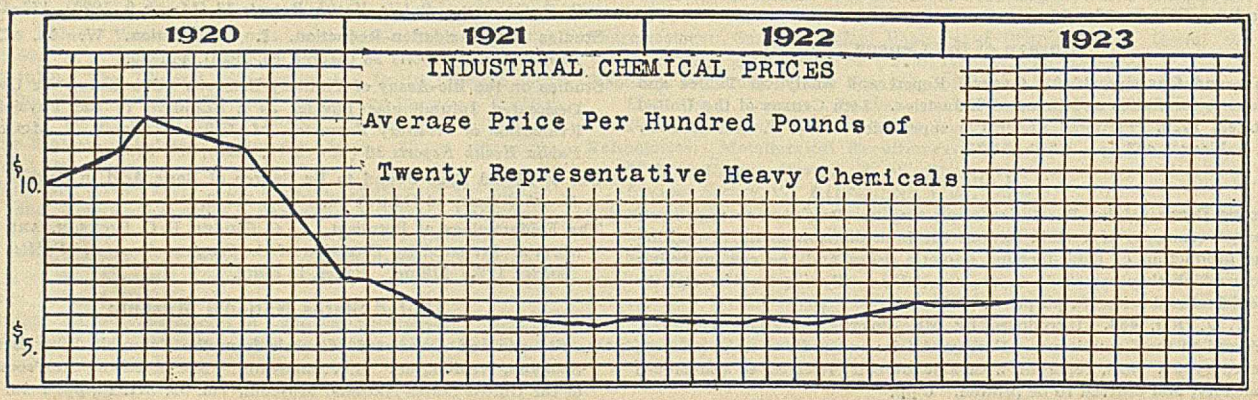
Imported chemicals have shown a tendency to advance in price, owing mainly to the scarcity and higher shipment prices. Offerings from Germany have been growing steadily smaller and higher in price. In many instances chemicals are now bringing higher prices in Germany than for export. Though stocks are said to be plentiful in the Ruhr district, nothing has come from that section since the German government prohibited the payment of a Ruhr export tax levied by the French. Potassium compounds have been advancing steadily. Potassium permanganate has advanced to 25 cents per lb. Caustic potash is selling at $8^1/_4$ to $8^1/_2$ cents per lb., with shipment prices at $8^1/_2$ cents per lb. Chlorate and bichromate are higher. Potassium bromide is higher. Prussiates have been quiet and prices easy. Ammonium chloride is scarce and higher.

With the exception of benzene, the entire list of coal-tar crudes are in small supply. Phenol made another sharp advance, jumping to 55 cents per lb. on an active demand and an acute scarcity of material. A small amount of cresylic acid is available, having been redistilled from imported crude material. The only xylol in the market is a small quantity imported from England. Toluene and solvent naphtha are very scarce. Seasonal demand has made naphthalene scarce and higher.

Consumption of intermediates has been increasing steadily and in some cases production is far from satisfying the demand. H acid is sold well in advance. Benzaldehyde is scarce. α-Naphthylamine is higher. Phenol derivatives have all advanced.

Linseed oil has been the strongest feature in the oil market. Demand for this product has been so great that with plants operating at capacity, crushers have been unable to supply all consumers. Prices have advanced to $1.20 per gal. China wood oil continues scarce and high. The market in miscellaneous oils and fats is strong, due to lack of offerings and an active demand.

Among the medicinal and fine chemicals, a steady interest has been noted with some prices still looking upward. The tartrates, especially tartaric acid and cream tartar, have become very scarce and prices have moved up steadily. American makers advanced quotations twice during the month, while it is well nigh impossible to buy goods abroad for import. Citric acid is in much the same position. Creosote, creosote carbonate, guaiacol carbonate, amidopyrine, antipyrine, and the benzoates are very strong. Salicylates are unchanged, but based on the phenol position are expected to go up further. Glycerol is easier and refiners have cut prices slightly. Heavy shipments of mercury from Europe have weakened the spot market. Bromides, both imported and domestic, are very strong. Makers of benzoates are unable to keep up with the demand.



Courtesy of Drug & Chemical Markets

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

INORGANIC CHEMICALS

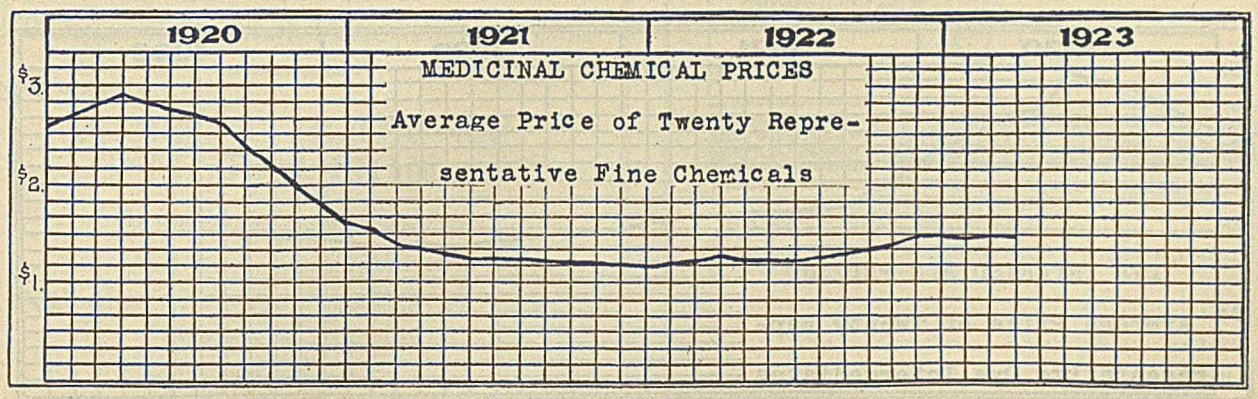
	Apr. 1	Apr. 15	Jan. 1923
Acid, Boric, cryst. bbls.....lb.	.11½	.11½	.11½
Hydrochloric,comm'l. 20°lb.	.01¼	.01¼	.01¼
Hydrofluoric, 30% bbls...lb.	.07	.07	.06
Hydriodic, 10% U. S. P...lb.	.65	.65	.65
Nitric, 42°, cbys. c/1 wks.lb.	.05¾	.05¾	.06
Phosphoric, 50% tech....lb.	.08	.09	.08
Sulfuric, C. P.....lb.	.08	.08	.07
66° tks. wks.....ton	15.00	15.00	15.00
Oleum, 20%.....ton	18.00	18.00	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.	.08	.08	.07¾
Ammonia, anhydrous.....lb.	.30	.30	.30
Ammonia Water, drums, 26°.lb.	.07½	.07½	.07½
Arsenic, white.....lb.	.15½	.15½	.15½
Barium Choride.....ton	*90.00	*85.00	*92.50
Nitrate.....lb.	*.08½	*.08½	*.07½
Barytes, white.....ton	33.50	33.50	33.50
Bleaching Powd., 35%, works .....100 lbs.	2.15	2.15	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.	.05¼	.05¼	.05¼
Copper Sulfate..... 100 lbs.	6.50	6.50	6.25
Iodine, resublimed.....lb.	4.55	4.55	4.50
Lead Acetate, white crystals..lb.	.13½	.13½	.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.	.01¾	.01¼	.01½
Oyster shell.....lb.	.03	.03	.03
Lime Acetate..... 100 lbs.	3.50	3.50	3.50
Magnesium Carbonate, tech..lb.	.08	.08	.08
Magnesite, calcined.....ton	55.00	55.00	55.00
Phosphorus, yellow.....lb.	*.28	*.28	*.28
Red.....lb.	*.45	*.45	*.30
Plaster of Paris, tech .....bbl.	3.30	3.30	3.30
Potassium Bichromate.....lb.	.11	.11	.10
Bromide, imported.....lb.	.16	*.16	.14½
Carbonate, calc.,80–85%.lb.	*.06	*.06½	*.05½
Chlorate, cryst.....lb.	*.07½	*.08	*.05½
Hydroxide, 88–92%.....lb.	*.08	*.08¼	*.08
Iodide, bulk, U. S. P.....lb.	3.75	3.75	3.60
Nitrate.....lb.	.06	.06	.06½
Permanganate, U. S. P...lb.	*.25	*.24	*.16
Prussiate, red.....lb.	*.80	*.80	*.90
Yellow.....lb.	*.37	*.37	*.38
Salt Cake, bulk.....ton	28.00	28.00	28.00
Silver Nitrate.....oz.	.43	.45½	.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

* Resale or Imported (not an American maker's price).

	Apr. 1	Apr. 15	Jan. 1923
Sodium Acetate.....lb.	.06½	.06¼	.07¼
Bicarbonate..... 100 lbs.	2.25	2.25	2.00
Bichromate.....lb.	.07½	.07½	.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.	3.25	2.90	3.60
Nitrate, 95%..... 100 lbs.	2.65	2.62	2.57½
Nitrite.....lb.	.09	.09	.08½
Prussiate, yellow.....lb.	.19	.19	.18½
Phosphate (di-sod.), tech.lb.	.03½	.03½	.03½
Silicate, 40°.....100 lbs.	.80	.80	.80
Sulfide, 60%, fused.....lb.	.05	.05	.05
Strontium Nitrate.....lb.	*.10½	*.11	*.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.	.13¾	.13¾	.10¼
Oxide.....lb.	.52	.52	.43
Zinc Chloride, U. S. P.....lb.	.20	.20	.20
Oxide, bbls.....lb.	.07½	.07½	.07½

ORGANIC CHEMICALS

	Apr. 1	Apr. 15	Jan. 1923
Acetanilide, U. S. P., bbls....lb.	*.35	*.35	*.35
Acid, Acetic, 28 p. c.... 100 lbs.	3.17½	3.17½	3.17½
Glacial.....100 lbs.	12.50	12.50	12.05
Benzoic, U. S. P.....lb.	.72	.72	.72
Carbolic, cryst., U. S. P., drs.....lb.	.47	.50	.32
50- to 110-lb. tins...lb.	.49	.52	.34
Citric, crystals, kegs.....lb.	*.50	*.52	*.48½
Oxalic, cryst., bbls., wks.lb.	.13	.13	.13½
Pyrogallic, resublimed...lb.	1.55	1.55	1.55
Salicylic, U. S. P.....lb.	.50	.50	.45
Tannic, U. S. P., bbls....lb.	.70	.70	.70
Tartaric, cryst., U. S. P...lb.	*.33½	*.35	*.32
Acetone, drums.....lb.	.22	.22	.21
Alcohol,denatured, complete. gal.	.41	.41	.45
Ethyl, 190 proof, bbls...gal.	4.70	4.70	4.70
Amyl Acetate..... gal.	3.50	3.50	2.50
Camphor, Jap, refined, cases .lb.	.90	.88	.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.	.40	.40	.40
Cresol, U. S. P.....lb.	.25	.25	.25
Dextrin, corn .....100 lbs.	3.39	3.54	3.09
Imported Potato.....lb.	.09	.09	.09
Ether, U. S. P., 100 lbs.....lb.	.13	.13	.13
Formaldehyde, bbls.....lb.	.15	.15	.16
Glycerol, dynamite, drums...lb.	.16½	.16	.16½
Methanol, pure, bbls.....gal.	1.30	1.30	1.35
Methylene Blue, med.....lb.	2.25	2.25	2.25
Petrolatum, light amber.....lb.	.03¾	.04½	.03¾
Pyridine.....gal.	2.75	2.75	2.75
Starch, corn, pow'd.....100 lbs.	2.82	2.97	2.47
Potato, Jap.....lb.	.05	.05	.06¾
Sago.....lb.	.04½	.04½	.03½



Courtesy Drug & Chemical Markets

OILS, WAXES, ETC.

	Apr. 1	Apr. 15	Jan. 1923
Beeswax, pure, white.....lb.	.36	.36	.36
Castor Oil, No. 3.....lb.	.14	.14½	.13
Ceresin, yellow.....lb.	.08½	.08½	.08½
Corn Oil, crude, tanks, mills...lb.	.10½	.10½	.09¾
Cottonseed Oil, crude, f. o. b. mill.....lb.	.10½	.10½	.09⅝
Linseed Oil, raw, lc/l.....gal.	1.10	1.20	.87
Menhaden Oil, crude, mills...gal.	Nom.	Nom.	.53
Neat's-foot Oil, 20°.....lb.	.18½	.17	.18½
Paraffin, 128–130 m. p., ref....lb.	.04	.04	.04
Rosin, "F" grade, 280 lbs....bbl.	6.30	6.30	6.25
Rosin Oil, first run.....gal.	.47	.47	.45
Shellac, T. N.....lb.	.81	.81	.80
Sperm Oil, bleached winter, 38°.....gal.	.99	.99	1.03
Stearic Acid, double pressed...lb.	.14½	.14½	.12½
Tallow Oil, acidless.....lb.	.11½	.11½	.11½
Turpentine, spirits of.....gal.	1.57	1.54	1.56

METALS

Aluminium, No. 1, ingots.....lb.	.24½	.24½	.23
Antimony, ordinary.....100 lbs.	8.75	8.87½	6.75
Bismuth.....lb.	2.75	2.75	2.75
Copper, electrolytic.....lb.	.17⅜	.17	.14¾
Lake.....lb.	.17½	.17¼	.14¾
Lead, N. Y.....100 lbs.	8.25	8.25	7.80
Nickel, electrolytic.....lb.	.25	.25	.36
Platinum, refined, soft.....oz.	118.00	118.00	118.00
Quicksilver, flask.....75 lbs. ea.	70.00	70.00	73.00
Silver, foreign.....oz.	.67⅛	.67⅛	.63
Tin.....lb.	.47¾	.46	.39
Tungsten Wolframite....per unit	8.50	8.00	7.50
Zinc, N. Y.....100 lbs.	8.00	7.75	8.25

FERTILIZER MATERIALS

Ammonium Sulfate, expt.100 lbs.	4.10	4.10	3.90
Blood, dried, f. o. b. N. Y...unit	4.75	4.75	4.70
Bone, 3 and 50, ground, raw..ton	32.00	32.00	28.00
Calcium Cyanamide, unit of ammonia.....	2.25	2.25	2.25
Fish Scrap, dried, wks.....unit	Nom.	Nom.	5.35 & .10
Phosphate Rock, f. o. b. mine:			
Florida Pebble, 68%.....ton	3.00	3.00	3.00
Tennessee, 78–80%.....ton	3.00	3.00	3.00
Potassium Muriate, 80%....unit	.68	.68	.70
Tankage, high-grade, f. o. b. Chicago.....unit	4.50 & .10	4.25 & .10	4.75 & .10

COAL-TAR CHEMICALS

	Apr. 1	Apr. 15	Jan. 1923
Crudes			
Anthracene, 80–85%.....lb.	.75	.75	.75
Benzene, pure, tanks.....gal.	.30	.30	.30
Naphthalene, flake.....lb.	.09	.09½	.06½
Phenol, drums.....lb.	.50	.55	.32
Crudes (*concluded*)			
Toluene, pure, tanks.....gal.	.30	.30	.30
Xylene, 2 deg. dist. range, drums.....gal.	1.00	1.00	—
Intermediates			
Acids:			
Anthranilic.....lb.	.96	.96	1.10
Benzoic, tech.....lb.	.70	.70	.65
Cleve's.....lb.	1.05	1.05	1.25
Gamma.....lb.	1.80	1.80	1.85
H.....lb.	.80	.80	.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.	1.25	1.25	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.	.17	.17	.17
Aniline Salt.....lb.	.24	.24	.25
Anthraquinone (sublimed).....lb.	1.30	1.30	1.30
Benzaldehyde, tech.....lb.	.65	.70	.65
U. S. P.....lb.	1.40	1.50	1.40
Benzidine Base.....lb.	.84	.84	.84
Benzidine Sulfate.....lb.	.70	.70	.70
Diaminophenol.....lb.	3.75	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.	.42	.42	.41
Dinitrobenzene.....lb.	.19½	.19½	.19
Dinitrotoluene.....lb.	.19	.19	.20
Diphenylamine.....lb.	.48	.48	.50
G Salt.....lb.	.55	.55	.60
Hydroquinol.....lb.	1.05	1.05	1.05
Monochlorobenzene.....lb.	.10	.10	.10
Monoethylaniline.....lb.	1.00	1.00	1.00
b-Naphthol, dist.....lb.	.24	.24	.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.	.90	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.	.35	.35	.35
R Salt.....lb.	.55	.55	.55
Resorcinol, tech.....lb.	1.50	1.50	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
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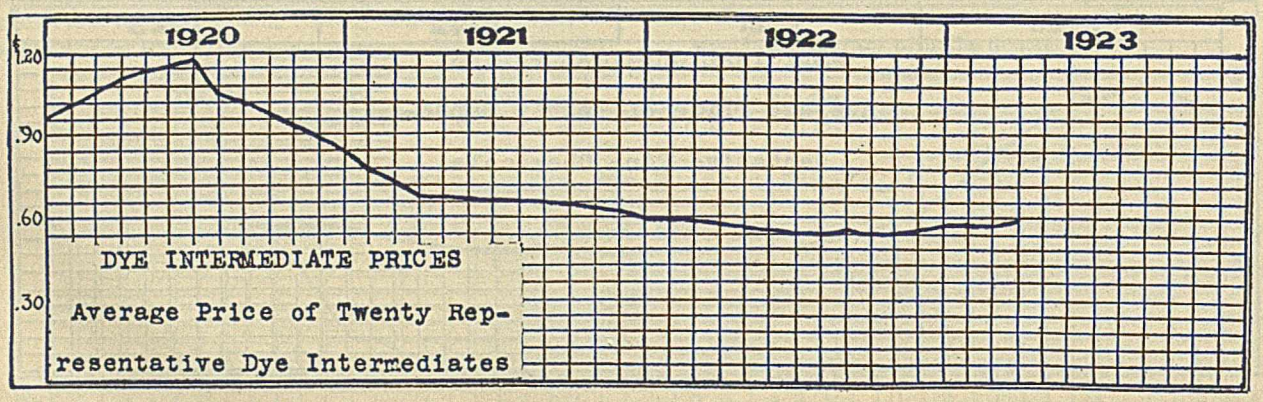

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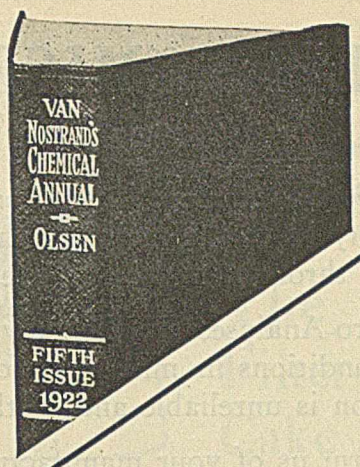

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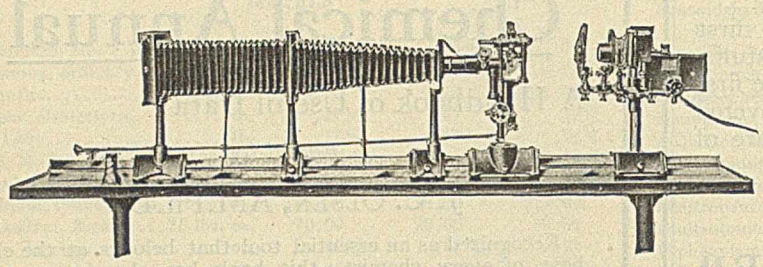

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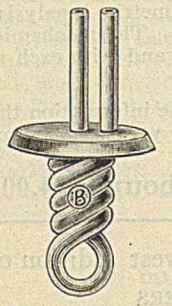

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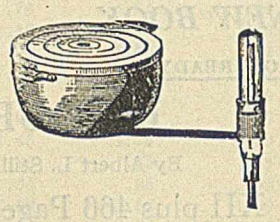

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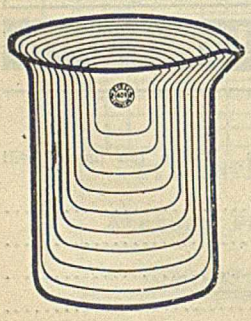

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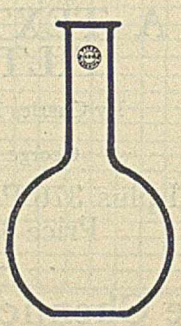

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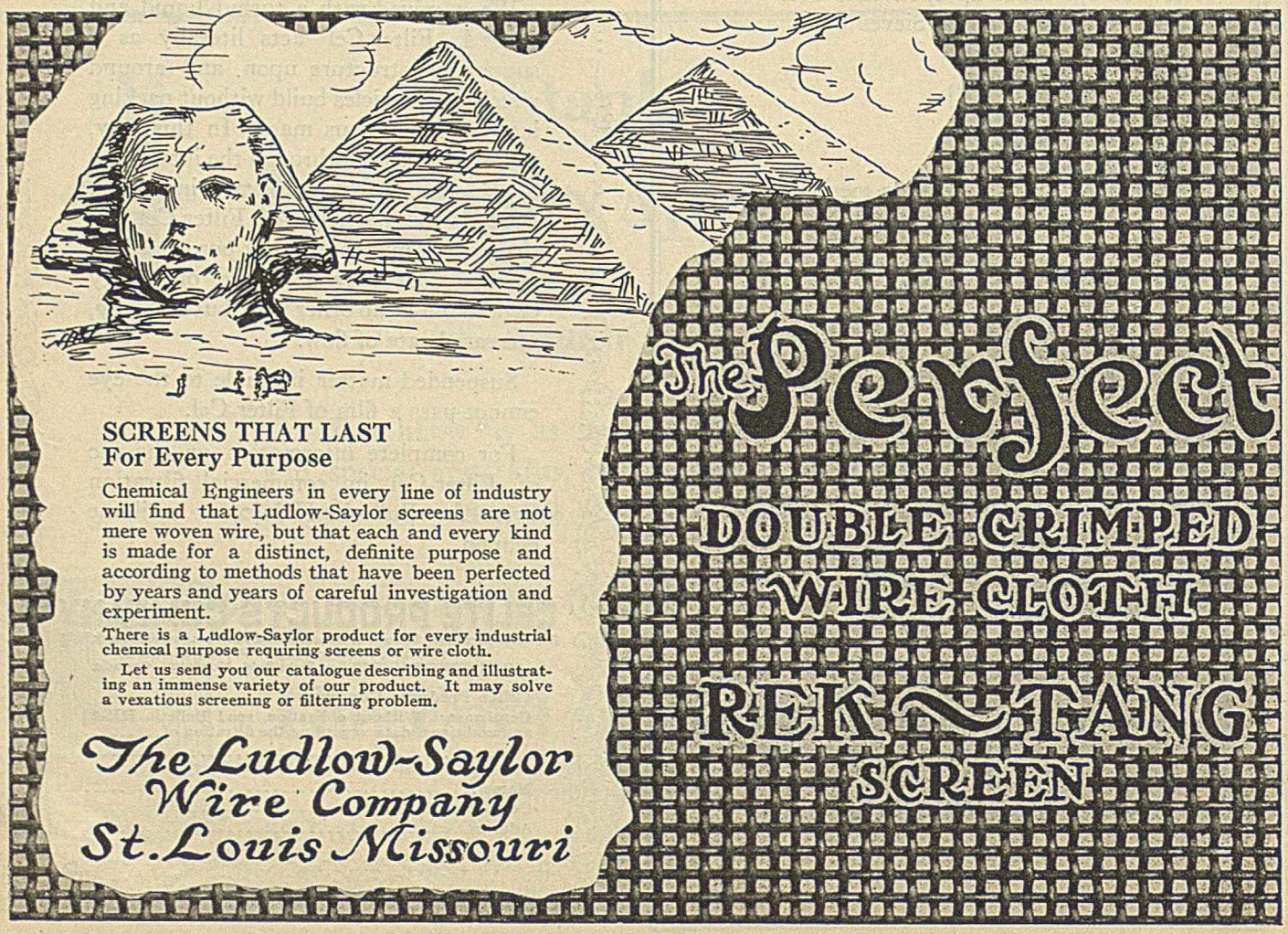
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