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EDITORIALS

Importation and an Opportunity

We have frequently been asked what are the present conditions under which apparatus and chemicals can be imported. To supply the answer we have made a careful investigation, and believe the results justify editorial comment.

It seems inadvisable to undertake importation of miscellaneous lists at the present time. Where highly specialized pieces of apparatus are required and the purchaser is prepared to take any and all risks involved, including annoying delays, there is, of course, more reason for importation than where miscellaneous lists for students are to be purchased at definite prices and for delivery at a specified time. We find that with the present German governmental control of glassware prices through export regulations, there is little, if any, price advantage in importing glassware, porcelain, etc., from that country. The time of delivery is most uncertain, while quality is often inferior to that of pre-war years. This matter of quality and workmanship applies both to apparatus and to chemicals. Much inferior apparatus has come in unmarked and is called American in case of complaint. One of the best known makes of reagents shows almost unbelievable deterioration as judged by recent lots, and we are informed that the actual management of the works has recently fallen into new hands. There is therefore little, if any, advantage in price, quality, or delivery. Last year one of our best known supply houses purchased only 6 per cent of its stock from Germany, despite the great advantage in exchange.

The present unsatisfactory condition under which importations can be made presents a wonderful opportunity to American manufacturers and to our dealers. There is also a need for constructive work on the part of the users. Let us treat these points in turn.

We need not rehearse the wonderful achievements of our manufacturers thus far. American manufacturers have made good in glass, in porcelain, in pyrometers, in hemacytometers, in electrical measurement apparatus, analytical balances, electric furnaces, electric ovens, all sheet-metal ware, all hardware, and a long list of devices which call for just as much ingenuity, resourcefulness, and persistence for their development as is the case with any chemical apparatus. Now is the time for American manufacturers to win all of the American and a share of the world market in face of foreign competition by the simple method of making the best apparatus at equal or lower prices if this is possible, but always the best. Many doubt whether the American market can ever be secured by American makers on a price basis. There are too many handicaps. Quality must be made the distinction. Americans cannot be expected to pay high prices for inferior material, but they soon learn the real economy of buying goods of quality. A large stock of a foreign glass lies unsalable in New York because even students have learned that in the long run an American glass is not only better but more economical.

In going about, we have heard of instances where manufacturers have not been willing to coöperate fully with users in providing glassware and other items in accordance with reasonable specifications. Manufacturers must go a little more than half way if the best results for all concerned are to be obtained.

The dealers have their opportunity in helping to place the purchase of large quantities on a really sound basis. Has the time not come when the man who buys an original package of apparatus or chemicals should have the lowest price for that package, regardless of the rest of his order? Why should a laboratory be given special consideration because of the size of a miscellaneous order over another laboratory which is willing to buy in standard packages? To the best of our knowledge, this condition does not obtain in other lines of business. The grocer who buys a barrel of sugar gets the lowest price on the barrel without regard to the number of boxes of raisins, prunes, and soap which accompany the order. Each item is priced on the quantity of that item.

Some dealers have also been somewhat responsible for present methods of buying by encouraging large laboratories to estimate in March what they will need in October. The result has been that many an institution has found itself with quantities of material lying idle in the stockroom, has bought unwisely except for a few standard items, and has in many cases practiced false economy. It would be an excellent thing for all concerned if the dealers would agree upon a sound business sales policy and seek coöperation of the large buyers in following out that policy.

It devolves upon the consumer to determine what is quality. For example, rubber manufacturers have come to know that many orders for tubing and stoppers are placed solely on the basis of price, and the maker finding the best way for introducing a high percentage of various fillers and substitutes gets the business. The result is that the best apparatus dealers can no longer depend upon regular stock production for laboratory use, but are compelled to have special tubing and stoppers made to insure uniformity and reasonable quality for the purpose intended.

And so with many other items in the list of 15,000 which make up the modern chemical apparatus catalog. Our Committee on Guaranteed Reagents and Standard Apparatus is doing constructive work of value. Might not that Committee or some other be charged with the duty of determining standards of quality as a protection to the purchaser and also to the faithful manufacturer and dealer who endeavors to give quality at a reasonable price?

The whole situation is after all an economic one. We have stated some of the factors involved. We can accomplish the best for all concerned if we can agree upon a working program. What is your experience?

The Freight Factor

Our chemical industry has been confronted with one handicap after another and has already overcome difficulties greater than those ever presented to other commercial enterprises. Among the difficulties which are common to industry in general, but which affect chemistry to an unusual degree, the freight factor is an example.

Other countries do not meet this difficulty. They are smaller, have consuming markets near production centers, or have the advantage of waterways like the Rhine. The sea enables many producers to deliver goods at a rate which practically stifles the corresponding American industry. Thus, grades of clay for certain porcelain insulators are brought from Wales at ten shillings per ton freight, while the same grades from American pits carry a freight of from nine to ten dollars a ton to consuming markets. One of the chief handicaps in selling American potash in the eastern consuming market is the freight item, which accounts for more of the difference in price between American and imported potash salts than the proposed tariff would compensate.

All industry goes back to power, and to-day the freight on some grades of coal is more than the same kinds of coal cost, delivered in factory bunkers, a few years ago. It is fairly well agreed that much of our freight cost is due to the fuel item and to wages paid railroad labor in excess of those paid the same class of labor in other industries. In the case of railroad labor, statistics will be helpful. The following figures are based upon data compiled by the Illinois Manufacturers Association:

There are approximately 380,000 employees who are directly concerned with train operations, and 1,341,000 workers who have nothing directly to do with trains. The latter are the shop craft labor, whose wages comprise nearly 80 per cent of the railway payroll. They are about 25 per cent overpaid, as compared with other industries. The figures show the following details:

	NUMBER	Average per Hour Quarter to June 30, 1921	Per Year 1920
Machinists..........	66,127	$ .883	$2,234
Boiler makers........	20,867	.893	2,314
Masons and bricklayers.............	1,210	.734	1,750
Blacksmiths.........	10,997	.874	2,119
Structural iron workers...............	715	.801	2,037
Carpenters..........	52,459	.758	1,808
Painters and upholsterers..........	13,201	.813	1,859
Electricians..........	15,247	(per day) 7.072	2,215
Airbrake men........	8,194	.845	2,141
Car inspectors.......	26,923	.847	2,313
Car repairers........	90,127	.819	1,997
Other skilled laborers..	60,526	.829	2,087
Mechanics helpers and apprentices........	139,298	.628	1,548
TOTAL SHOPMEN...	505,891		
Section men.........	276,829	.451	1,179
Enginehouse men.....	76,993	.54	1,527
Other unskilled laborers.............	121,197	.520	1,306
TOTAL.............	980,910		
Clerks..............	243,965	.701	1,647
Station service.......	116,968	.546	1,373
GRAND TOTAL.....	1,341,843		
Trainmen			
YARD EMPLOYEES			
Engineers...........	23,747	.93	2,650
Firemen.............	23,923	.73	2,005
Conductors..........	23,513	.89	2,514
Brakemen...........	58,548	.83	2,265
Switch tenders.......	6,779	.64	1,795
Others..............	5,088	.54	1,436
ROAD TRAINMEN			
Freight engineers.....	35,717	1.154	3,436
Firemen.............	38,590	.875	2,452
Conductors..........	29,027	.977	3,008
Brakemen...........	72,203	.776	2,331
Passenger engineers...	13,190	1.369	3,326
Passenger firemen....	12,724	1.053	2,475
Passenger conductors.	11,070	1.148	2,971
Passenger baggagemen	5,899	.863	2,240
Passenger brake and flagmen...........	16,291	.847	2,094
Others..............	3,711	.663	1,775
Total.............	380,120		
Hostlers.............	12,439		
GRAND TOTAL.....	392,120		

These figures show that the so-called common skilled labor such as is employed in the repairing of freight cars receives an average of 84 cents an hour, while the prevailing rate in the manufacturing industry is about 45 cents an hour. No one can object to the wages paid those who have in their care not only such expensive equipment as locomotives but the safety of many lives, but it does seem unnecessary to burden business in general by the payment to other classes of labor of such wages as these statistics show. Many an instructor in our educational institutions and no small percentage of professional men look upon these annual earnings with a little wistfulness. It seems unlikely that transportation costs can be brought back to normal unless some adjustments can be made in the wages of some classes of railroad labor. When this is done the chemical industry will be encouraged, along with other manufacturers.

The Tariff Bill

The following extract is taken from the Report to accompany the tariff bill (H. R. 7456), which was submitted to the Senate by the Chairman of the Finance Committee on April 11, 1922.

DYES AND SYNTHETIC ORGANIC CHEMICALS

It was found that the rates provided for dyes and coal-tar chemicals, after the limited embargo provisions covering these products had been eliminated on the floor of the House of Representatives, were wholly inadequate to protect the domestic industry.

It is common knowledge that Germany had a monopoly of the world's trade in dyes prior to the war. Although our domestic industry has made great strides during and since the war, when these products have been admitted to the United States only under license, as provided by the emergency tariff act of May 27, 1921, and although our industry is capable of supplying between 85 and 90 per cent of the quantity required of domestic consumers, it has not attained a point in efficiency of manufacture where it can hope to compete with the well-organized industry which exists in Germany. Your Committee has reached the conclusion that no rates in American tariff history would be adequate to protect this industry.

Your Committee therefore recommends that the provisions of the emergency tariff act relating to dyes and synthetic organic chemicals be extended for a period of one year after the tariff bill becomes a law. In subdivision (*d*) of Section 315 the President is also authorized, if upon investigation he ascertains that the rates specified upon coal-tar intermediates and dyes do not equalize the differences in competition here and abroad, or if he ascertains that an industry in the United States is being or is likely to be injured by reason of the importation of like intermediates or dyes into the United States, to issue a proclamation stating such fact and to continue the dye and chemical control act in force for a further period not to exceed one year. In addition, the following rates of duty on these products are proposed: 50 per cent plus 7 cents per pound on intermediates and 60 per cent plus 7 cents per pound on finished coal-tar products. Under the administrative provisions of the bill, the President has been given authority to base these rates on American values of similar competitive articles and also to increase or decrease the rates not exceeding 50 per cent, if, after investigation, he may find such action necessary. The extension of the dye control provisions of the emergency tariff act for one year (and two years if necessary) will give the President sufficient time to investigate conditions in the domestic dye and coal-tar industry, to ascertain what products can be protected by the rates specified in this bill, to determine the products on which it will be necessary to assess duties based upon American valuation, and to decide what increase in rates will be necessary in order that all branches of this industry may become firmly established in the United States.

It will take courage to go forward with development on a large scale under this bill. A great gain has been made, however, in the matter of time. This can be used to advantage in making sure that a larger proportion of Congress becomes familiar with the conditions involved.

Technical Information Service

Organizations of business men are wont to establish a variety of services designed to the profit of the members of the group—legal, taxation, insurance, accounting, banking, and freight are subjects usually receiving special consideration. But it has remained for the Associated Industries of Massachusetts to establish a technical information service for its members. This is a forward step of direct interest to chemists and establishes a precedent which should assist chemists in other localities in bringing home to manufacturers a realization that in applied science they have a reliable anchor to windward.

New England has been a favorable place for such activities because of its relatively small area, the concentration of its diversified manufacturing, and the agencies at work. The several colleges and universities and technical schools have been active centers, aided by several commercial laboratories. When one chemist does a really good piece of work, all chemists and the science are directly benefited. If the work is poor, all suffer. We quote from the Association's announcement:

> The service is equipped to answer inquiries on the fundamental processes employed in manufacturing operations, such as steam generation, water softening, lubrication, heating, drying of materials, filtration, distillation, evaporation, dyeing, etc., and to supply members with knowledge which will be of material aid in solving problems of construction, the properties of building materials, the selection of the more important types of equipment for certain operations, the erection of machinery, and the like. It is also in a position to direct members to sources of information on technical subjects and to places where materials or equipment can be obtained to the best advantage.

This is an encouraging sign which should be brought to the attention of business organizations everywhere.

Is a Commercial War between Chemists and Business Men Coming?

The United States to-day abounds in chemical knowledge. If the business men do not utilize it properly, the chemists themselves will.

Chemical advice, dearly purchased and highly praised during the war, is now being shelved and disregarded. Perhaps it is only a coincidence that at the same time trade is stagnant, and our hold on foreign markets dwindling.

Hundreds of chemists, vainly looking for positions, will probably be forced to engage in business for themselves. Thus fate may push them into good fortune, and the skeptical business men out of it.

All further talk about the good that chemists can do for manufacturers is wasted. A baker, refusing to take advantage of chemical knowledge, may some day wake up to find that a chemist has opened a bakery shop on the other side of the street. It may easily happen that he will be convinced and bankrupted at the same time.

Chemical knowledge, like many other desirable goods, will not be bought by the public unless it is sold to them. Triumphant competition may eventually be the slogan of a successful although painful selling campaign.

The kind of goods that sells on merit only, without selling effort, is yet to be found. Chemists have relied entirely on the merit of their goods, and have not sold them; manufacturers have refused to believe that anything not advertised on billboards can have merit. As a result, both sides have suffered severely.

Chemists, inclusive of college teachers, need to learn that even an all-wool suit will not sell if a dealer puts it into a dark basement.

Most chemists spend their lives advising manufacturers how to make money. Napoleon was an adviser to two helpless generals at the siege of Toulon, and, while he kept on advising, Toulon held out. One day, Paris instructed Napoleon to take charge, whereupon he carried out his own advices and Toulon fell.

If chemists have as much faith in their advice as they claim they have, they will stop fretting and fuming about the incompetence of business men; they will start to compete with the business men and show them how.

The business men may have to worry about this, but the public will not. They will get their goods better, cheaper, and more uniform than ever before.

Otto Eisenschiml

Distribution of Chemists

Data compiled by the Association of Harvard Chemists throw light upon the distribution of a typical group of men who have concentrated in chemistry while at that institution. The data are based upon letters sent to 950 men, of whom 628 replied. An analysis of the returns shows that 157 of these men are teaching in various colleges, three having reached the grade of president; 38 are teaching in high schools; 40 are graduate students in chemistry; 35 have become physicians and surgeons; 43 are in the employ of the Government; 103 are executives in commercial chemistry; 159 are commercial chemists; and 41 in purely commercial work. In the latter class we find 15 in accounting and finance, 4 in manufacturing and sales other than chemistry, 5 editors and publishers, 9 patent attorneys, and 1 governor of state. Classification of executives in commercial chemistry is as follows: 15 presidents, 10 vice presidents, 4 secretaries, 5 treasurers, 23 managers, 23 superintendents, 8 assistant superintendents, 2 chemical foremen, 3 purchasing agents, 8 sales managers, and 2 salesmen.

Among other things, the above figures indicate the diversity of work which a chemical training makes possible. We believe that if similar figures were available for men who specialized in other sciences, it would be found that chemistry is in an enviable position.

The Earning Power of Research

Aside from chemical control in making the very dense and brilliant lead glass blanks used in making cut glass, chemistry formerly had little to do with producing the finished product. All operations were mechanical. Patterns were marked out on the blank, and steel wheels, with mitered edges and armed with trickling sand and water, were used to make the deep cuts and the finer tracery. Stone wheels next smoothed the roughly cut surfaces. Wooden wheels with pumice and water gave an approach to a polish, and finally rapidly revolving brushes with putty powder (tin oxide) gave the high finish. The men who operated these four types of apparatus were all highly skilled and highly paid. About 1895 attempts were made to utilize the action of hydrofluoric acid on glass, in order to eliminate the two final processes almost entirely. Many difficulties were encountered by the chemists who attempted to control this reaction. Finally, however, they were overcome, and one or two men can now polish the output of a large factory, permitting the laying off of perhaps forty highly paid workers and the selling to the public of fine cut glass ware at much less than it could otherwise be marketed.

As in all such cases the advance is hard, for the time being, on the men laid off, but they eventually do something else for the world, and society in general benefits from the advance.

Frank B. Wade

When Muscle Shoals is leased, it will be in order to make an all-American fertilizer. Phosphoric acid by electric furnace methods from supplies of phosphate rock near at hand suggests itself. American potash is seeking a market. Nitrates will be made on the spot. Such a scheme for a concentrated complete fertilizer sounds feasible, and an all-American fertilizer surely has advertising possibilities.

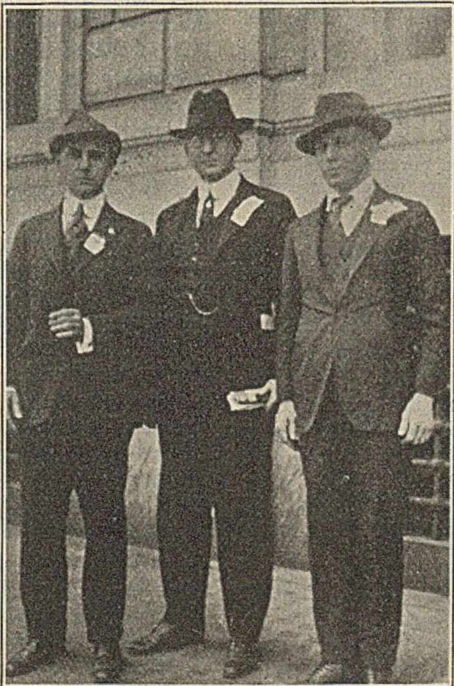
BIRMINGHAM MEETING AMERICAN CHEMICAL SOCIETY

An unusual opportunity to meet fellow chemists and discuss problems of mutual interest, interested discussion of good papers, and a really uncommon industrial excursion—these were the outstanding points of our spring meeting. The attendance, while less than 400, was made up of representatives from 35 states, from Canada, and one visitor from the far-away isle of Mauritius. The geographical distribution of those in attendance showed the following at the top of the list in the order mentioned:

Alabama	51
New York	33
Illinois	32
Ohio	31
District of Columbia	29
Pennsylvania	26

The Local Committee, though laboring under a number of handicaps, did everything possible to make the meeting an unqualified success, and Chairman J. F. Carle with his immediate staff of assistants earned our sincere thanks. The Alabama Technical Association were our hosts at the smoker, while the Tennessee Coal, Iron and Railroad Company contributed to our profit and pleasure to a very great degree.

The Society was really complimented when the First Methodist Church after due consideration made available their Sunday school rooms for the Division and Section meetings. So far as we know it is the first occasion upon which a church has been used for such meetings of our Society, and it was the first occasion upon which meetings of a non-religious character had been permitted in this edifice. The balance was swung in our favor by the fact that the church authorities recognize the efforts of chemists to ascertain the truth.



Some Members of the Local Committee
Max Kuniansky, J. F Carle, J. T. MacKenzie

The short distance between the hotel headquarters and meeting places, together with the time allotted upon the program, gave us an unusual opportunity to meet the men and to have time to talk things out. There is no question that chemistry in the South was greatly stimulated by the meeting. The press was generous in its notices of our activities, and because of our visit it will be possible for the achievements of chemistry to be kept before the people by the efforts of the press and those chemists who are willing to tell of their work. The meeting also served to call popular attention to the efforts of chemists who are combining business ability with technical knowledge in the utilization of southern resources.

The excursion upon the 7th deserves particular mention. It might even be called a symposium upon iron and steel. In one day we were shown the mines and quarries necessary for the support of blast furnace and steel mills, the furnaces, the rolling mills turning out their various types of steel products, mills for fabricating steel, the production of wire, nails, fencing, etc.

In the hope that those expecting to attend the autumn meeting may read these lines, we would emphasize the importance of those traveling by rail to the meetings obtaining certificates when tickets are purchased and bringing these tickets for certification to the meeting. This should be done without regard to whether the purchaser expects to return by the same route or not. Those traveling to Birmingham probably lost $3000 because there were insufficient certificates to entitle the holders to half fare on the return. Had all those who attended from a distance presented certificates, this substantial saving could have been made.

At the General Meeting, following the warm words of welcome from Lieut. Gov. Miller and the representative of the City Commissioners, Dr. Ellwood Hendrick read a tribute to the work of Dr. Baskerville, and Dr. W. A. Noyes presented a statement concerning the work of the late Ciamician. He also paid tribute to the work of von Baeyer and Emil Fischer, obituaries of whom are to appear in the *Journal* of the Society.

Before opening the scientific part of the morning's program, President Smith referred briefly to the activities of the Local Sections which have most impressed him on his visits during the past year. The coöperation of the Rochester Section with the city Chamber of Commerce, in such economic welfare work as procuring pure pasteurized milk for the city and exterminating rats and other dangerous pests, is only one example of what this active Section is doing in bringing before the public the value of this most essential science. The monthly publications of the Sections, he said, are an index of those who conduct these enterprises. For example, the *Bulletin* of the Chicago Section is breezy, and also homey, and holds out the welcome hand. There is a decidedly wholesome, earnest, scientific atmosphere. He urged a broad knowledge of chemistry. "The more we know of it in its strange and marvelous appearances the better for us. It may be analytical, agricultural, organic, physical, electro, etc., but it is *chemistry*, and the broader our training and equipment the more readily will we be able to follow it in its many varieties. Let us 'prove all things and hold fast to the good.' Let us be *chemists*, with contempt for no one of the forms it may assume in the hands and under the guidance of minds of honest, broadly trained devotees of the science."

Once more it has been demonstrated that meetings of the Society can be held with great success at some distance from the center of population or where the Section is not large, but where encouragement to local members of the Society and the advancement of our profession in the locality fully repay the effort involved.

The Council Meeting

About 80 men gathered for the Council Meeting on the evening of April 3 at the Southern Club. In his introductory remarks, made in his well-known happy style, Dr. Smith called attention to the slight regard given the technical experts at the recent conference for the limitation of armament, and noted the present status of the dye embargo. The Secretary then presented a letter from the Chemical Foundation, which was received with profound thanks from the Council on behalf of the SOCIETY. The letter follows:

FEBRUARY 27, 1922

Dr. Charles L. Parsons,
Secretary of the American Chemical Society,
Mills Building, Washington, D. C.

DEAR DR. PARSONS:

I have read your letter of January 10 and sincerely regret that the AMERICAN CHEMICAL SOCIETY, because of lack of funds, has been compelled to stop the publication of the Formula Index and to cut down considerably in the publication of scientific and industrial chemical literature. This retrenchment will be a real blow to the advancement of chemistry in this country, because chemical progress is fundamental to the health and industrial development of the country.

In order that the work of the AMERICAN CHEMICAL SOCIETY may continue without interruption, the Chemical Foundation will supply the money needed to print the Formula Index and to cover the retrenchment which the Directors thought necessary up to $25,000 for the year 1922.

Very truly yours,
FRANCIS P. GARVAN

In this connection attention was particularly called to the importance of increasing the membership of the SOCIETY. While recognizing that chemists have had the same embarrassments as other folks during the last year or so, it is nevertheless true that from the number who are interested in chemistry in this country it ought to be possible for us to draw a sufficient membership to make it unnecessary to seek support from other sources for our activities. There is no question that industry shows a trend for the better, and chemists should watch their opportunity to gain additional members for the SOCIETY.

President Smith then presented the report of the Priestley Fund Committee, details of which appear on p. 458. A letter from the Patent Commissioner thanking the SOCIETY for its efforts in forwarding the work of the Patent Office was presented, and then came the welcome news that the first two monographs published for the SOCIETY by the Chemical Catalog Company had not only paid their way but had earned certain dividends for the SOCIETY. There is reason to believe that the entire series will be very successful from all viewpoints. A resolution was adopted that publishers of chemical books be asked in the future to indicate the date when books are written or revised, citing these same dates in announcements concerning the volumes. It is obvious that the printing date is of far less importance to scientific men than the date when the copy was actually prepared. The resolution will be brought to the attention of the publishers.

The Cellulose and Petroleum Sections, having asked to be made Divisions, were advised that when by-laws to be presented at the Pittsburgh Meeting had been approved, they would be advanced to the status of Divisions. The Council then voted that in the future Sections would be required to go through a probation period of three years to demonstrate the justification for their formation and the likelihood of their being able to continue in active work before they would be recognized as Divisions. The request for the formation of Local Sections in Hawaii and at Sacramento were granted. The Morgantown, W. Va., request was approved, subject to waivers being given by the Pittsburgh Section and to a possible change in name to avoid future complications. After extended discussion as to whether or not the SOCIETY favored the formation of Local Sections in foreign countries it was decided that no change should be made for the present.

The invitation from the New Haven Section for the spring meeting of 1923 was accepted by unanimous vote. The invitation of San Francisco for late July or early August 1923 was then presented, and the advantages of California were rehearsed in a unique manner by Dr. E. C. Franklin, who told of a few things which are not to be found in California, the claims of enthusiasts to the contrary notwithstanding. Professor R. E. Swain, who had come from the coast for the meeting, urged the acceptance of the invitation when the time comes for the vote. The possibility of our being invited to Ithaca upon the completion of the new laboratory in 1923 was also announced, and President Smith put on record the invitation of Philadelphia for the autumn of 1926, that being the fiftieth anniversary of the formation of the SOCIETY and the time of the sesquicentennial exposition to be held at Philadelphia. Prof. William McPherson was elected a member of the Advisory Committee to succeed H. E. Howe. Prof. Henry Clay White of the University of Georgia, Athens, Ga., was felicitated for his fifty years' continuous service in the department of chemistry at that university.

The Council passed a resolution that at each semiannual meeting of the SOCIETY announcement should be made of the names of donors who had made grants for the promotion of research in chemistry, not only in recognition of their generosity but for the purpose of calling the attention of others to the desire for such grants in an ever-widening field. A motion to instruct the Directors as to the activities which should be restricted in case the budget exceeds the expected income was laid on the table. The status of student members was then discussed, several feeling that because of the increased costs of printing to the SOCIETY, the dues of student members ought to be advanced in conformity with advances made in the dues of the SOCIETY. It was decided, however, to make no change at this time.

Authority was granted to delete the words "the journal of" from the name of the *Journal of Industrial and Engineering Chemistry*, so that beginning with the January 1923 number this journal will be known as *Industrial and Engineering Chemistry*. The President was authorized to appoint a committee of seven to consider a number of suggestions that have been made relative to the activities of the SOCIETY and its various officers and committees. Some have suggested that perhaps our Directors should be elected from specified regions; that a change should be made in the method of electing members of the SOCIETY; that a group of fellows of the SOCIETY should be created, to be elected by the Council for meritorious work in chemistry. These and other suggestions will be considered by the committee which will endeavor to report at the Pittsburgh Meeting. The Council then voted to reaffirm its former decision with respect to intersectional meetings, encouraging these meetings wherever it may be possible to hold them, particularly for the benefit of the younger men who find it inconvenient to attend the spring and fall meetings of the SOCIETY and who deserve an opportunity to present their papers before larger groups than their Section meetings.

The final discussion of the Council had to do with our employment problem. (Report is printed in full on p. 456.) By a very close vote the Council went on record as favoring the establishment of an employment agency which would be especially interested in the chemist, but by an overwhelming vote thought this activity should not be under the auspices of the AMERICAN CHEMICAL SOCIETY. A committee was authorized to confer with other professional men who are now working upon this same question. There were many who felt that the university and the Local Sections have in the employment question an unusual opportunity for service to their chemists. In addition to these activities the need for a central clearing house and coördinating agency was expressed.

The Flower and the Organic Chemist: Perfumes—Natural and Synthetic

By Marston Taylor Bogert

Columbia University, New York, N. Y.

De gustibus non disputandum est is nowhere more clearly applicable than in the field of perfumes. "One man's spinach is another man's poison ivy." An odor highly pleasing to certain individuals may be exceedingly disagreeable to others. The dictionary's definition of a perfume, as "the scent emitted from a sweet-smelling substance; a pleasant odor," therefore does not help us to standardize perfumes, or to prove that all odors which please you and me belong *ipso facto* in that category.

In the absence of any absolute standard of reference, we must fall back upon the verdict implied in the extent of the demand for the different odors and the price which such perfume substances command; a verdict which naturally will vary considerably from year to year, for there are fads and fashions in this field as in others, and will not be identical in different countries, or even among different classes of the population in the same country.

In man, the olfactory cells are located in a recess in the upper back portion of the nasal cavity, away from the direct air current to the lungs. These cells have fine hairlike tips reaching to the surface of the mucous membrane lining the cavity and exposed to the chemical stimuli of odors, while backward from their bases extend long slender sensory nerves which pass through the bone and into the skull chamber and brain stem, there connecting through their end-brushes with the dendrites of nerve cells, whence the stimulus travels to the olfactory area of the cortex, there to be received, interpreted, and the information utilized or filed. These olfactory cells are unique among vertebrate sense cells in being provided with their own sensory nerves, instead of depending upon the sensory axon of an ordinary nerve cell.

To stimulate this organ and produce the sensation of smell, particles of the substance must be brought into actual physical contact with the hair tips of these cells in the mucous lining, either carried by a current of air or by diffusion of the vapor, dissolving in the moisture of the olfactory epithelium and there reacting chemically with the nerve tips; from which it follows that only such substances can possess an odor as are at least partially volatile at the temperature of observation. It has been shown, however, that liquid carriers may also be used, and that odor may be detected when odoriferous substances are dissolved in saline, or other suitable menstrua, and taken into the nostrils. This, of course, suggests the possibility of a stimulus to the olfactory sense by a solution whose solute is itself too difficultly volatile to give off any perceptible fragrance at ordinary temperatures. It is worth noting that in such cases the odor varies with the concentration of the odoriferous substance in the liquid, being quite different in strong solutions from what it is in dilute ones. The theories which postulate odor as due to a form of motion of the ether, and its transmission as similar to that of sound or light, appear to be without any convincing experimental proof.

The olfactory, or first nerve, is hard to investigate because its receptive surfaces are intimately associated with those of the fifth nerve, which is a nerve of common sensation (tactile). For this reason, true smells, *i. e.*, those substances which stimulate the olfactory only, are hard to separate from pungent substances, like vinegar, which stimulate the fifth nerve as well.

For these reasons, Beaunis arranged all substances which affect the olfactory mucous membranes in three groups:[1]

1—Those which act only on the olfactory nerve—(*a*) pure scents, or perfumes, without pungency; and (*b*) odors with a certain pungency, like menthol.

2—Those which stimulate simultaneously both olfactory and tactile nerves, like acetic acid.

3—Those which stimulate only the tactile nerves, like carbon dioxide.

Zwaardemaker,[2] who has studied the subject both extensively and intensively, recognizes nine classes of pure odors, corresponding to Beaunis' first class, which he designates as follows:

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1—Ethereal, or fruity; characteristic in general of the fruits, and due in most cases to the presence of various esters; including also beeswax, and certain ethers, aldehydes and ketones.

2—Aromatic, which is further divided into:

- (*a*) Camphoraceous: borneol, camphor, eucalyptol.
- (*b*) Spicy: eugenol, ginger, pepper, cinnamon, cassia, mace.
- (*c*) Anise-lavender: anethol, lavender, menthol, thymol, safrol, peppermint.
- (*d*) Lemon-rose: geraniol, citral, linalyl acetate, sandalwood.
- (*e*) Amygdaline: benzaldehyde, oil of bitter almonds, nitrobenzene, prussic acid, salicyl aldehyde.

3—Fragrant, or balsamic, composed of:

- (*a*) Floral: jasmine, ylang-ylang, orange blossoms, lilac, terpineol, lily of the valley.
- (*b*) Lily: lily, tuberose, narcissus, hyacinth, orris, violet, ionone, mignonette.
- (*c*) Balsamic: vanillin, piperonal, coumarin, balsams of peru and tolu.

4—Ambrosial: musk and amber. This odor is present in the flesh, blood and excreta (referable to the bile) of certain animals.

5—Alliaceous, or garlic: onion, garlic and many compounds of S, Se, Te and As; and subdivided as follows:

- (*a*) Alliaceous: hydrides of S, Se and Te, mercaptans, organic sulfides, thioacetone, asafetida.
- (*b*) Cacodyl-fish odors: hydrides of P and As, cacodyl compounds, $(CH_3)_3N$.
- (*c*) Bromine odors: Br, Cl, I, quinone.

6—Empyreumatic, or burnt: as in tar, baked bread, roasted coffee, tobacco, benzene, naphthalene, phenol, and products of dry distillation of wood.

7—Hircine, or goat: due in the case of this animal to the caproic and caprylic esters contained in the sweat, and typified also by perspiration and cheese.

8—Repulsive: such as are given off by many of the narcotic plants and by acanthus.

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[1] Stewart, "Textbook of Physiology."

[2] "Physiologie des Geruchs," **1895**, 233.

9—Nauseating, or fetid: as given off by products of putrefaction (feces, etc.), and by certain plants.

Unfortunately, we have no words to represent shades of odor, as we have for colors.

The psychologists, as the result of Henning's investigations, incline to the opinion that there are but six elementary odors:[3]

1—Spicy, found in pepper, cloves, nutmegs, etc.
2—Flowery, found in heliotrope, etc.
3—Fruity, found in apple, orange oil, vinegar, etc.
4—Resinous, found in turpentine, pine needles, etc.
5—Foul, found in hydrogen sulfide, etc.
6—Scorched, found in tarry substances.

and that all others are made up of blends of these six in varying proportions.

Dr. Septimus Piesse maintained that inasmuch as every perfume produces its own peculiar effect upon the olfactory cells, just as every musical note has its own characteristic action upon the ear, therefore all odors can be arranged in a scale or gamut, corresponding to the musical scale; and he actually constructed such a scale of perfumes, each note of the musical gamut having its corresponding perfume, the heavy odors (patchouli, vanilla, etc.) representing the low notes, and the sharp odors (peppermint, citronella, etc.) the high ones. This he termed his "odophone," and asserted that no proper blend could be made unless the component perfumes harmonized in the scale. Thus, the chord of C, for example, would constitute a harmonious blend.

The organic chemist's method of attack upon this problem of classification of odors will be explained a little later. Most of us rest content with just two classes: agreeable and disagreeable.

No sense is more marvelously delicate than that of smell, nor is any more potent in awakening our memories and our emotions. Some people may be indifferent to music, but those unaffected by odors are rare indeed. A breath of perfume brings instantly before our vision past scenes with all their pain or pleasure. Kipling recognized this when he wrote: "Smells are surer than sounds and sights, to make the heart strings crack." From certain odors we recoil instinctively, not because they are intrinsically unpleasant, but because of the associations they recall; while others, perhaps unattractive to our fellows, possess a peculiar fascination for us. The recognition of a perfume is practically instantaneous, as is the picture it conjures up. It is like suddenly glimpsing a familiar face in a passing crowd.

The olfactory cortical center in the hippocampal lobe is known to be widely connected with other parts of the cerebrum, and this probably explains the extensive associations connected with odors, and the excellence of our olfactory memories. In animals like the dog, with highly developed olfactory organs, and among the invertebrates, it is intimately connected with the sexual reflexes, and some remnant of this relationship is found in the human organism. Comparative anatomy reveals the interesting fact that phylogenetically smelling is the oldest sense of all, and it is also true that it gives pleasant or unpleasant sensations in a more marked and general way than either sight or hearing. Of the so-called special senses, it appears to be the one most closely connected with animal appetites, and Howell[4] is led to remark that "over-gratification or over-indulgence of this sense, according to historical evidence, has at least been associated with periods of marked decadence of virtue among civilized nations."

It is also one of the senses particularly susceptible to "adaptation," *i. e.*, a diminution or cessation of the sensation in spite of the continuance of the stimulus, a phenomenon probably akin to fatigue. Both individuals and odors show widely divergent behavior in this respect. Some odors quickly fatigue or benumb the sense of smell in nearly all persons; whereas, with other smells, only a few individuals will gradually lose their ability to detect them while remaining in the same atmosphere.

Drugs that act centrally may stimulate or depress the sensation. Thus, strychnine and caffeine stimulate it, while choral depresses it. The application of cocaine to the nasal mucous membranes totally paralyzes the sense of smell. In disease, changes in the nerve may occur, occasionally resulting in total loss of this sense (anosmia).

The actual amount of an odor which can be clearly perceived by man is in many cases exceedingly minute. Camphor is detected in a dilution of one part in 400,000; musk in 1:8,000,000; vanillin in 1:10,000,000. Vallentine found that 1/120,000 of a grain of oil of rose was all that was necessary; while Fischer and Pentzoldt determined that 1/460,000,000 of a milligram of mercaptan was the approximate minimum amount coming into contact with the olfactory nerves and immediately recognized by them. The pleasant odor of the soil was ascribed by Berthelot, the distinguished French chemist, to traces of an unidentified camphoraceous body, of so powerful a fragrance that even a trillionth of a milligram gave a clearly perceptible smell.

In man, the acuteness of the sense varies widely. Some few individuals appear to lack it entirely, *i. e.*, are smell-blind. It is perhaps surprising to find that, on the average, it is much more delicate in males than in females. By practice, it may be extraordinarily developed, as we see in our own North American Indians, and in some African races and aboriginal tribes, who can track enemies almost like a hound. Among practical perfumers, it is also found cultivated in high degree, especially on the analytical side. A blend, which the layman thinks is a simple perfume, is recognized immediately by the expert as a composite, many or all of whose elements are entirely familiar to him.

One of the beneficent provisions of Nature consists in a sharpening of other senses when some one sense is lost. It is Nature's way of doing her best to compensate for the damage suffered. A group of humanitarian Parisian perfumers are engaged in training men who were blinded in the war to become experts in evaluating odors, not only as a measure of reconstruction, but also in the well-grounded belief that a blind man, freed from any distractions associated with vision, should make a perfumery expert of the first rank.

Yet more amazingly acute is this sense in other members of the animal kingdom. The ability of dogs to follow a scent to which the human nose is wholly blind is a familiar example, as is also the scenting of hidden carrion by vultures at incredible distances. Pliny affirmed that carrion crows have so keen a sense of approaching corruption that they can scent death three days before actual dissolution, and hence sometimes pay the moribund a visit before his time, to avoid disappointment. This is perhaps the origin of the popular superstition that such a visit forebodes death.

The shark, which is among the more active and intelligent of the fishes, has an olfactory membrane which, if spread out, would cover some 12 square feet.

Many insects are strongly odoriferous, and the odors emitted are nearly always disagreeable. Insects also possess a remarkably developed sense of smell, the olfactory organs being located mainly or exclusively on the antennae, in the form of specially modified sense hairs, or sensillae, which are particularly highly developed in insects with the sharpest sense of smell (*e. g.*, in ichneumon flies). Huber has shown that bees are greatly excited by the smell of their own sting poison, and that they dislike musk, but have no aversion to asafetida. Bomare's experiments indicate that the friendly bedbug (*Cimex lectularius*) is attracted, not as popularly supposed by the warmth of the couch, but by the scent of his victim. It is not unlikely that other human parasites and insect enemies, *e. g.*, mosquitoes,

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[3] Woodworth," Psychology," 203.

[4] "Physiology," 305.

gnats, etc., also locate their prey similarly in the dark. The *Arum dracunculus* bears a large liver-colored flower, and exhales a stink which is so fetid and carrion-like that blow-flies, carrion flies, and other slaughter-house frequenters are said to mistake this flower for putrid meat and flock to it from all directions there to deposit their eggs.

Some of the most interesting researches are those which have been conducted with ants,[5] insects which can perceive odors either diffused in the air or dissolved in liquids. The tactile and olfactory sensillae are so closely associated on the antennae that when the latter actually touch an object, the ant probably receives both tactile and olfactory stimuli simultaneously, which Forel believes fuse to a single sensation and which he calls the topo-chemical, or contact-odor sensation, and endows the ant with a sense of odor-shape. He explains this by suggesting that we imagine ourselves either blind or in total darkness, but possessed of exceedingly delicate olfactory organs in our finger tips. As we moved about, then, touching various objects, our environment would appear to us to be made up of odors of different shapes, and we would speak of spherical perfumes, oblong stinks, etc. Our mental processes would be governed by a cosmos of chemical configurations, just as they are now by a world of visual (*i. e.*, color) shapes. As ants spend most of their time in the dark recesses of the nest and rely but little upon their eyesight, it is evident that their mental processes must be quite different from our own. These insects also exhibit remarkable powers of odor-discrimination and odor-association, enabling them not only to distinguish the smells characteristic of species, caste, sex, and individual, as well as the adventitious odors of the nest or surroundings, but also (according to Miss Fielde) even progressive odors, due to the changing physiological condition of the individual with advancing age, a refinement which in the case of humans might save us many complications and embarrassments.

The use of sweet-smelling substances appears to have originated in religious worship, to which service they were for some time wholly consecrated, and it is from Persia that we first hear of them. The caravan which carried Joseph captive into Egypt was engaged in this traffic between the latter country and Persia. Alexander the Great, after his defeat of Darius, found in the latter's camp great treasure of perfumes and precious salves.

Among the Jews such material was consecrated to the church, and in the Bible several passages occur where they are rebuked by their prophets for using them upon the person. Sweet balsams and gums are frequently mentioned in the life of our Saviour. At His birth, frankincense was offered Him by the Wise Men, later Mary annointed His feet with precious ointment, and after His crucifixion Joseph of Arimathea placed His body in the tomb with balm and sweet spices. It was this custom which originated our word "embalm."

The Greeks always described their gods as being redolent of ambrosia and, according to their mythology, man would have had no knowledge of perfumes had it not been for the indiscretion of Oenone, one of the nymphs of Venus. As early as 300 B. C., Appolonius wrote a treatise upon perfumes, in which he speaks of essence of rose, iris, and others, mentioning the localities producing the finest quality. The Athenians even had special perfumes for various parts of the body—palm oil for the cheeks and breast, mint for the arms, marjoram oil for the hair and eyebrows, thyme for the neck and chin, but the odor of the violet was prized most highly by them, even as it is with us at the present day. The use of perfumes became such a craze that the perfume shops of Athens were the general rendezvous, where matters of state were discussed, fashions talked over, and stories exchanged, and it was just as natural for an Athenian woman to say "Meet me at the perfumer's," as it would be for a New Yorker to say "Meet me at the theater." At fashionable entertainments the rooms were often perfumed, and occasionally trained doves, whose wings had been previously wetted with the most delightful essences, were allowed to fly about, the vibration of their wings raining perfume down upon the heads of the assembled guests. Solon finally proposed a law restricting the sale of perfumes, so that none should be sold to men, at least; and Socrates bitterly complained because the slave and the freeman, when perfumed, smelt exactly alike.

From Greece, the use of perfumes traveled to Rome, where it was similarly abused. Thus, it is said that Nero, at the funeral of his wife Poppaea, used more perfumes than all Arabia then furnished in a whole year. Pliny raised his voice against such excessive use, and under the Consul Licinius Crassus a law was passed restricting the use of perfume substances, so that the churches should not lack. It is amusing to read that Plancus, proscribed by the triumvirs and pursued by their soldiers, took refuge in a cave, but his hiding place was betrayed by the perfume issuing therefrom.

The overthrow of Rome obliterated the commerce of Europe, and perfumes disappeared from the Continent until brought back by the Moors from Arabia. In this latter country, their use had never ceased, and whole districts were devoted to raising flowers for this sole purpose. The "black-eyed houris" of the Koran, were not to consist of ordinary flesh and blood, but "of purest musk." The Arabian physician Avicenna, in the tenth century, practiced the art of distilling perfumed waters; and in the twelfth century rose water, and possibly others also, was available in large amount, for on the entry of Saladin into Jerusalem, in 1157, the walls of the Mosque of Omar had been previously washed with it.

From the settlements of the Moors, the use of perfumes spread to France, where it soon became general and lavish, reaching its climax at the court of Louis XV, where the royal rooms were perfumed each day with a different odor, and where it was deemed an act of gallantry for a courtier to use the favorite perfume of the lady he courted, just as the knight carried his lady's colors.

Perfumes are said to have been introduced into England by the Count of Oxford, who brought some from Italy in the fifteenth year of the reign of Queen Elizabeth, and their use appears to have been carried to extremes there also, for in 1770 the English Parliament passed a law which provided that "any woman, of whatsoever rank, profession, or condition, girl, woman, or widow, who, subsequent to the date of this Act, shall deceive, entice, or influence to marriage, any of Her Majesty's subjects by the aid of Perfumes, False Hair, High Heels,*****, shall be subject to the same penalty as that now in force against sorcery, and the marriage shall be declared void and of no effect."

To-day the use of perfumes has spread over the world, and has extended to all classes of the community, with a steadily increasing demand. It has given birth to an independent and important industry, regulated mainly, it is true, by fashion and the taste of the consumer, but which nevertheless gives employment to thousands of men, women, and children, urges on the botanist to search for new plants containing odoriferous oils or resins, busies the engineer with devising new machinery for their extraction, and gives to the chemist the fascinating problem of determining the composition of these perfumes and of reproducing or imitating them in his laboratory.

The animal kingdom supplies us with but few valuable aromatics, musk, civet, castor, and ambergris being the only important ones. By far the greater number come from plants, where they occur as the volatile or essential oils, or as the gum resins. The essential oils are contained in various parts of the plant: sometimes in the wood, as santal, cedar, etc.; the bark, as cinnamon and cassia; the leaves, as patchouli, bay, thyme; the flowers, as rose, lavender, violet, tuberose, etc.; the fruit, as lemon, citron, nutmeg; or the seeds, as almond and caraway. As examples of gum resins, on the other hand, we have storax,

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[5] See W. M. Wheeler's "Ants."

Carlile P. Winslow, Edgar F. Smith, Ellwood Hendrick, H. C. Parmalee, R. B. Moore, W. D. Collins, Rev. George L. Coyle, William H. Stone, J. A. Steffens

benzoin, tolu, opoponax, olibanum, the latter being the gum usually burned as incense.

The essential oils and other odoriferous constituents are usually obtained from the plant by one or more of the following processes:

MECHANICAL METHODS—In some few cases, the essential oil is present in such large amounts that it can be separated by simple mechanical means. This is true of the essential oils found in the peels of lemons, and of the sweet and bitter oranges. The oil cells may be ruptured by pressure, manual or mechanical, or by perforation with sharp instruments. The process in vogue in Sicily and southern Italy, where labor is cheap, is the "spugna," or sponge process, the peels being turned inside out by hand while pressing against an ordinary sponge. The inversion of the peel breaks the oil cells, and the oil and moisture contained squirts out into the sponge, instead of into the eye of the operator. As the sponge becomes saturated, it is squeezed out, the yield averaging about 1.5 pounds of oil per man per day. In the United States, where labor is high, power presses have been used for recovering citrus oils in California.

The "ecuelle" process of Northern Italy utilizes a saucer-shaped vessel, 8 to 10 inches in diameter, and studded inside with short spikes or knives about one-quarter inch long, and with a half-inch hole in the center, opening into a hollow tube handle some 4 or 5 inches long. As the fruit is rotated in this saucer, the oil cells are punctured and the oil flows down and collects in the hollow handle. Apparatus has also been devised for carrying out the same process mechanically on a large scale.

DISTILLATION WITH STEAM—The proper part of the plant is placed in a still and distilled in a current of steam. This steam may be generated outside the still and passed into it, or water may be added direct to the still contents and the steam generated by boiling the same, or the two methods may be combined. As the steam passes over, it carries with it the essential oil, and the two are condensed and collected together. Insoluble oils or constituents separate from the water in the distillate, while the soluble portions remain in solution in the aqueous layer. Not infrequently, sufficient of the perfume is thus held in the aqueous distillate to render the product of economic value. "Rose water" is such a by-product separated from the insoluble oil or attar of rose.

This is the process by which the vast majority of essential oils are obtained, and is applicable to practically all, although not always giving the best results. It is an economical method, both from the standpoint of the labor involved and the simplicity of the apparatus required, unless the oil present is easily soluble in water, or is relatively small in amount. Further, it is not satisfactory where the perfume substance is itself affected by the steam, as is true with most of the flower aromas. For such odors, one of the following processes is customarily employed.

EXTRACTION WITH VOLATILE SOLVENTS (petroleum ether, benzene, etc.), comprising the four steps:

1—Selection and purification of the solvent.

2—Systematic extraction of the flowers in batteries of extractors.

3—Evaporation of the solvent, leaving a vegetable wax saturated with the perfume (*cire parfumëer*).

4—Recovery of the solvent.

The extracts left after evaporation of the solvent, known also as "concretes," are shaken with strong alcohol, which dissolves out the perfume, these tinctures being then called "floral extracts" (*extraits aux fleurs*). By separating the pure flower oil from its solution in the alcohol, the "quintessences" are obtained.

Using petroleum ether as solvent, the yields of concretes run somewhat as follows, per ton of flowers:

Victoria violets	3.0 to 3.6 lbs.
Roses	3.4 to 5.0 lbs.
Orange blossoms	4.0 to 8.0 lbs.
Jasmine	3.2 to 4.5 lbs.
Cassie	7.0 to 10.0 lbs.
Mignonette	2.6 to 3.0 lbs.

In addition to the flowers mentioned above, extraction with volatile solvents is applied also to tuberose, jonquil, and occasionally to carnations, lily of the valley, heliotrope, narcissus, mimosa, and others.

A disadvantage under which it sometimes labors is the fact that the other substances also extracted by the solvent may affect unfavorably the fine quality of the perfume.

MACERATION, INFUSION, OR ENFLEURAGE À CHAUD—The housewife knows to her sorrow with what avidity butter and other fats, as well as milk (on account of the butter fat it contains), imbibe odors of any kind in the refrigerator, and this property is utilized by the practical perfume manufacturer to collect the aroma from the flowers.

In the maceration, or warm absorption process, the flowers, either in bulk or in fine linen sacks, are soaked in warm (50° to 70° C.) oil or molten fat (lard, tallow, olive oil, etc.) until the perfume is all removed, when the fat is separated, by pressing or centrifuging, and fresh flowers added to it, the operation being repeated (six to fifteen times) until the fat is thoroughly saturated with the perfume. The duration of this digestion varies from comparatively brief periods up to forty-eight hours; generally, the longer the digestion, the greater the yield, but the lower the quality. Fats thus impregnated with perfume come into the market under the name of "pomades," the perfume being then extracted from them by treatment with strong alcohol.

The process is used with violets, roses, orange blossoms, lily of the valley, and some others, but not with jasmine, tuberose, or jonquil, on account of the low yields and inferior quality.

ENFLEURAGE À FROID, OR COLD ABSORPTION—The perfume exhaled by the jasmine, tuberose, jonquil, lily of the valley, and mignonette is best collected by the cold absorption or enfleurage process, the aroma being taken up by thin layers of cold fat or wax. The mixture generally used in southern France consists of 40 per cent beef fat and 60 per cent lard, except in the hottest part of the season, when a 50:50 mixture is preferable. Both fats must be purified with the most scrupulous care, as the character of the resultant pomade depends first and foremost upon the quality of the fats.

The mixture is spread to the depth of about one-eighth inch upon both sides of glass plates which are supported in the middle of open wooden frames, or "chassis," two inches deep, and twenty to thirty-two inches square. The flowers, freed from their calices, are spread over the layer of fat on one side of the glass plate, crisscross furrows having been made previously in the fat, so as to increase the surface exposed.

The frames filled with flowers are then piled up, one on top of the other, in stacks as high as the operator can reach conveniently, thus leaving the flowers enclosed in shallow compartments, the perfume exhaled being imbibed by the fat upon which the flowers repose and by the layer upon the under surface of the glass plate immediately above. The length of exposure varies, being 24 hours for jasmine, 48 for jonquil, and 72 for tuberose. The last named must be placed upon the fat in the unopened condition and there allowed to expand, or it will be spoiled by the next day. After suitable exposure, the flowers are removed, the frames turned upside down, and fresh flowers spread on what was previously the under side of the glass plate, and the frames then stacked up again. By thus alternating the surfaces carrying the flowers, a more even distribution of the aroma in the fat is accomplished. For high-grade pomades, the fat must be exposed to at least thirty different changes of fresh flowers. Where liquid oils are used, instead of solid fats, the glass plates of the chassis are replaced by wire screens which support woolen cloths saturated with the oil.

As before, the perfume is extracted from the pomade with strong alcohol, the small amount of fat so dissolved separated by freezing, and from these purified extracts the essences are recovered by removal of the alcohol.

From the standpoint of the perfume manufacturer, flowers fall into two classes: (1) Those, like the rose and orange blossom, which contain their perfume ready made and immediately available in full amount; and (2) those, of the jasmine and tuberose class, which when first picked appear to contain but small amounts of essential oil, but keep on producing it continuously as part of the life functions of the cell. If flowers of the latter group are treated with steam or hot solvents, they are killed and the further production of perfume ceases; but when the cut bloom is placed over cold fat, it continues to live for many hours and to give off perfume uninterruptedly. So, Hesse[6] found that ten times as much perfume was recovered from jasmine flowers by the cold enfleurage process as by extraction with volatile solvents; in the case of the tuberose, the difference is still greater.

In flowers of the first group, however, larger yields are often secured by the other methods. In the case of orange blossoms, for example, it has been shown[7] that a ton of blossoms yields only 0.2 pound of flower oil to cold enfleurage, whereas maceration gives 0.8 pound, and distillation with steam 2.4 pounds, in the latter case 0.8 pound of this total remaining dissolved in the aqueous portion of the distillate.

For centuries, southern France, with its balmy climate and mountain barriers against the cold winds of the north, has been the world's most famous region for this industry, having succeeded to the position occupied in ancient times by Arabia and its surrounding territory. Even the early Romans were accustomed to bring perfumes from Gaul, and under Louis XII France's export trade in such material was firmly established. Reference has already been made to the lavish use of perfumes at the court of Louis XV, where Mme. de Pompadour is said to have spent 50,000 francs per annum, a fabulous sum in those days, on perfumes alone.

The French Revolution banned such substances totally, but as the years rolled by the wealthier classes resumed their use, and by the beginning of the nineteenth century this use had extended to the middle class also. Since then the development of the industry has been rapid, until to-day its export trade is in excess of three hundred million francs, and is an important contributor to the prosperity and happiness of the French people.

The little city of Grasse, with some twenty thousand inhabitants, in the Alpes-Maritimes Department of Provence, is the heart of the flower-growing district, with a dozen well-known firms and numerous smaller ones, and is really one vast flower garden.

In Grasse alone, the consumption of flowers for the past ten years has averaged in tons per annum:

Orange blossoms	2200	Tuberoses	330
Roses	1650	Carnations	165
Jasmine	1320	Cassie	110
Mimosa branches	880	Mignonette	66
Violets	440	Narcissus	55

In 1898, orange blossoms brought 6 cents per pound, roses 5.5 cents, jasmine 22 cents, cassie flowers and violets 35 cents, and tuberoses 45 cents; but prices have been rising steadily since, and in 1917 (on account of the war) reached 18 cents per pound for orange blossoms and over 30 cents for roses, with other flowers in like proportion. The combined value of the 1917 Grasse harvest of these two flowers alone therefore amounted to nine and one-quarter million francs, or about $1,850,000 at normal exchange.

To produce the 1320 tons of jasmine flowers noted above, at least 750 acres are required, representing some thirty million plants. An orange tree yields about 22 pounds of blossoms, and a violet plant one-twenty-fifth of a pound. A pound of orange blossom oil (oil neroli petal) requires about 1000 pounds of blooms, *i. e.*, the total output of over forty-five trees, or approximately 500,000 separate flowers; while, in the case of the oil or attar of rose, eight tons, or two and one-half million roses, are necessary to yield one pound of the attar. The justification for what seem like exorbitant prices for the highest grade perfumes is thus clear.

In the Department of the Var, adjoining Grasse to the west, some seventy-five hundred acres are devoted to raising violets, hyacinths, mimosa, roses, carnations, lily of the valley, and other flowers, giving employment to eight thousand people, and with an annual output worth between three and four million dollars.

In a large factory, it is not unusual at the height of the season to receive in a single day twenty-two tons of roses and a similar amount of orange blossoms, all of which must be treated immediately before fading; so that men, women, and children work from dawn to midnight during this strenuous period of two or three weeks.

The annual output of lavender oil in southern France has been one hundred tons, worth $600,000; of spike lavender oil, twenty-five tons, worth $50,000; and of geranium oil, five tons, worth $40,000.

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[6] *Ber.*, **34** (1901), 293, 2928; **36** (1903), 1465.

[7] Hesse and Zeitschel, *J. prakt. Chem.*, [2] **64** (1901), 245.

Nearly all of these essential oils are mixtures, and not infrequently contain nonodorous components. They may be used direct, or may themselves be subjected to such treatment as will isolate the more valuable aromatic constituents or remove the inert ones.

The methods for accomplishing this are either physical or chemical.

I. PHYSICAL METHODS. (*a*) *Freezing*—Odoriferous components are often separated thus from essential oils, and the method has the advantage of not changing in any way the quality of the substance so isolated. Safrol can be so recovered from oil of sassafras, anethol from oil of anise, and menthol from peppermint oil. It is a process which is also used occasionally to remove inert constituents (stearoptenes) from such flower oils as the attar of rose, thus effecting an indirect concentration of the odoriferous portion.

(*b*) *Distillation with steam*, to free the more volatile from the less volatile compounds.

(*c*) *Fractional distillation under reduced pressure*—Many substances which cannot be distilled at ordinary atmospheric pressure without decomposition, boil unchanged when the pressure is diminished sufficiently.

(*d*) *Sublimation*, which amounts to a slow distillation of solids, and is applied in the case of camphor, for example.

(*e*) *Crystallization*, which is the process employed for most solids.

II. CHEMICAL METHODS—(*a*) Acidic compounds may be extracted by aqueous solutions of alkali carbonates, and the acid subsequently liberated from the alkali salt.

(*b*) Phenols are dissolved out by caustic alkalies.

(*c*) Alcohols are often isolated as esters (of phthalic, succinic, or benzoic acids), the esters purified and then saponified.

(*d*) Aldehydes and certain ketones may be combined with $NaHSO_3$.

(*e*) Basic compounds are removed by treatment with dilute acids.

(*f*) Specific reactions are frequently utilized: geraniol forms a compound with calcium chloride, carvone combines with hydrogen sulfides, eucalyptol with phosphoric acid, etc.

(*g*) Methods which will destroy or remove the contaminants without injury to the constituent sought. Thus, in fennel oil the anethol is rapidly oxidized by pure concentrated nitric acid, while the fenchone is practically unattacked; geraniol is not changed by alkalies, but any citral present is thereby polymerized to higher boiling compounds; citronellol is esterified normally by boiling formic acid, but other terpene alcohols are decomposed or dehydrated by it.

The composition of most natural perfumes is now known, at least approximately, to the organic chemist. Some he has been able to reproduce exactly, others he can but imitate. It is his firm conviction that the stimulus imparted to the olfactory nerve tips is due to a definite chemical reaction between the substance of which these nerves are composed and the molecules of the odoriferous compound, and he has endeavored to ascertain whether these compounds have anything in common chemically to which this action may be ascribed. As in the case of the synthetic dyes and synthetic drugs, he has endeavored to fasten the blame upon certain definite groupings of the atoms present in the molecules, and has even christened such groups "odorophores," "osmophores," or "aromatophores." He will tell you that a carbon compound containing one or more such groups in its molecule, if sufficiently volatile at ordinary temperatures, is very likely to possess a definite odor, but what will be the character of the aroma he cannot always foretell so accurately, although even in this direction he has made noteworthy progress. When you see a steeple in the distance, you recognize a church; but only a closer inspection will disclose the particular denomination to which it belongs.

The fascinating nature of this problem lies not only in the discovery of one of Nature's closely guarded secrets, for the perfume has been well termed the soul of the flower, but with this information once in his possession he will be able not alone to duplicate any natural floral essence, but also to build up any number of new ones at will. Already many perfume substances are in common use which, so far as we are aware, do not occur in nature. They are made in man's laboratory, instead of in that of the plant. Many of the well-recognized constituents of essential oils are now produced also by the organic chemist, and the products so obtained are in no respect inferior to the natural article. His lines of attack have been twofold. In some instances, the initial substance has been a natural product, perhaps a perfume itself, which he has transformed by the magic of his art into a more valuable one (*e. g.*, asafetida into vanilla). In other cases, the results are true synthetics, built up step by step from simpler substances, in general obtained from coal tar. The transmutation of this foul black mass into delicious perfumes is one of his miracles, akin to his production of dyes of all the hues of the rainbow and of life-restoring drugs from the same unpromising raw material. Even that deadly war gas, phosgene, has come out from under his hands as a beautiful new violet perfume (methyl heptine carbonate).

Both natural and synthetic products are required by the modern toilet perfume manufacturer. They constitute his raw materials, and are to him what the pigments are to the painter. The preparation of a really fine blend is the work of the expert, and in that occupation he is as truly creating a work of art as are his fellow artists of the brush and chisel. The price which milady's perfume commands is determined therefore not alone by the cost of its ingredients, but also by the skill with which they have been selected and combined to form one harmonious whole.

Informational Needs in Science and Technology

By Charles L. Reese

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

THERE is a common saying that "Knowledge is Power." Information and knowledge are so closely related that it might be said that information is power, and coördinated information is power plus. The rapid rate at which knowledge has been and is being accumulated, particularly in science and technology, is brought out very forcibly by the Polish engineer Korzybski in his remarkable book, "Manhood of Humanity," and it seems that extraordinary steps must be taken to coördinate and correlate information in such a way as to make it available to all capable of using it throughout the world.

Efficiency in research and in the application of its results is significantly conditioned by command of information. To the individual, nation, or race which most skilfully, thoroughly, and wisely masters and uses the accumulated knowledge of mankind comes supremacy in industry, if not also in science, politics, and art. Creators of knowledge through the application of scientific method to Nature are prone to belittle or to ignore the devices by which information is conserved, rendered conveniently accessible, and disseminated. Rather it becomes us to inquire whether by giving systematic attention to means of marshaling and using what has been discovered, invented, felt, imagined, constructed, we may not render uniquely valuable service to civilization.

Time was when knowledge was transmitted from man to man or generation to generation either orally or by rude products of human labor. Then came written language and, finally, printing, libraries, and the construction of such keys to knowledge as catalogs, indexes, handbooks, encyclopedias. All the while the rate of accession to information has increased rapidly, although irregularly. Man has become increasingly a thinking animal with remarkable development of curiosity, resourcefulness, originality, breadth of interest and view, foresight, disinterestedness, and sympathy. With multitudes of individuals and generations feverishly active, often progressive, all striving to live more comfortably, happily, usefully and longer, and to command Nature more successfully to these ends, what are the chances that my present idea, thought, or plan is new—shall we say one in a million? It requires but scant attention to the matter to convince us that the efficiency of our use of the products of human thought and of its records is astoundingly low. We chemists are continuously repeating not only mental processes but, as well, the experimental procedures of our predecessors in research. Within limits this duplication of labor is desirable and profitable, but how far we fall short of utilizing as we should the constructive efforts of those unnumbered generations of men and women whose lives prepared the way for ours.

Charles L. Reese

The progress of discovery and invention has nearly eliminated space as a barrier between individuals and peoples. Time, it has been compressed. The output of carefully recorded information is to-day overwhelmingly large—the world is producing millions of printed, typed and written pages of records of research, invention, development, and practical experience, not to mention cultural and esthetic creations. This amazing increase in the quantity of human knowledge is accompanied by corresponding increase in specialization of interest, occupation, and terminology. Tongues also have multiplied, and mental patterns, human needs, and demands have become more diverse. In general, as knowledge has increased, the devices for handling it have become less satisfactory. Few needs are now clearer or more urgent than the construction of efficient informational mechanisms or keys to knowledge. The question I present to you is, "How may the constructive agencies in science and industry help to bring about the designing and installation of suitable informational mechanisms?" May we not profitably bring our scientific method, habit of mind, purpose, and need to bear on this important problem with a view to devising informational master-keys which shall render human knowledge many times more available and, therefore, more valuable?

It is obvious that knowledge, even in a relatively narrow field, has outgrown the capacity of most individuals. However encyclopedic we may be by nature or training, we can master only certain fragments of the information which mankind has accumulated. It is conceivable, however, that we should be able to construct an informational system which would enable every reasonably intelligent and fairly well-educated person to obtain the essential information about a given subject when needed. Why should we not handle the packing, storage, shipping, and distribution of knowledge as efficiently as we manage commercial production? We have gradually devised a system of exchange, national and international, which with reasonable satisfactoriness enables us to enjoy the products of others' skill and industry. Such systems are imperfect, but by comparison with present modes of preserving information and rendering it accessible to posterity, they are highly advanced.

Largely because knowledge is discontinuous and relatively unavailable, history repeats itself endlessly and tragically. Ignorance, it would appear, is responsible for more catastrophes and racial setbacks than are carelessness, selfishness, and maliciousness combined. The solemn duty rests on us to devise adequate ways and means of carrying forward always, with continuously increasing accessibility, the sum of useful knowledge and experience. The fact that the task has not been done is good evidence of its difficultness, not of its impossibility or its lack of importance.

DEVELOPMENTS DURING THE WAR

The World War at once revealed some of the weaknesses of our informational position and our ability to remedy them. When the tremendous need for munitions and men came we were plodding along self-satisfied and generally oblivious of the fact that we commanded relatively little information. Almost over night, investigators and industries became aware that knowledge, conditions, discovery, invention, production—in a word, efficiency of effort was lacking. Intelligence bureaus, informational departments, staffs of abstractors, indexers, compilers, and purveyors appeared suddenly all over the country. What Germany had at hand in 1914, because of her superior foresight and appreciation of the supreme value of systematized available knowledge and of the indispensableness of research, we were compelled to try to create at high speed and with feverish haste. It is enlightening to examine some of our information-seeking activities in their relation to our present need and opportunity.

COMMERCIAL ACTIVITIES—My own company, when it undertook a number of new lines of manufacture, beginning during the latter days of the war, recognized the need of more extensive and more comprehensive information along these lines. An Intelligence Division was therefore organized, charged with the collection, integration, and dissemination of technical information on the subjects in which we were interested. At the time of its maximum activity this Division was spending $80,000 per year for salaries alone, and comprised a personnel of thirty-five men and women.

A classified index of the dye patents of the United States was prepared; foundations were laid for a general information catalog, which, while no longer being added to at the present time, is still a valuable library tool; an information index of our research reports was started and is just being completed; a library was organized, etc. While many of the activities of the Division probably were of interest only to the du Pont Company, it is unquestionably true that some of the activities could better have been carried on by some organization like the Research Information Service of the National Research Council, and the results would then have been available to the country at large.

For more than five years the Chemical Catalog Company has conducted an information bureau for the benefit of chemical industry and its personnel. Informational demands increased so considerably that it was found desirable in 1921 to place this bureau on a charge basis. A fee of $25 per year is now charged to firms or individuals who wish to command the service. This also, it should be noted, is a highly specialized service limited to chemical technology and making no special provision for information concerning research.

The National Industrial Conference Board, organized and maintained by the industries of the country, is one of the most active and efficient intelligence agencies in the country. Their activities are mostly along industrial, social, and economic lines, and they have made since 1917 forty-five research reports and twenty special reports as a result of studies on such subjects as changes in cost of living, strikes, works councils, profit sharing, health service in industry, taxes, hours of labor, and metric versus English system of weights and measures. All of these are the results of the collection of statistics and the presentation of facts.

These instances of informational activities directed toward increasing the availability of commercially valuable information are typical of what has been achieved or attempted for various industries throughout the United States since 1917. Many of the informational bureaus which sprang up by reason of war needs have been abandoned because of economic pressure. Others are struggling to achieve self-support and profit. The indications are clear, however, that a general informational clearing house should be an endowed public service organization, independent alike of the need of self-support and of gain.

GOVERNMENTAL WORK—Of governmental informational activities certain notable instances should be mentioned. The Food Administration perfected a staff and statistical machinery which provided it with unprecedentedly complete intelligence concerning food production, distribution, consumption, waste, and prices. The statistical department of the Food Administration, as was generally recognized during the war and has since been made clear by its reports, functioned with marvelous efficiency as an intelligence agency.

With a view to enabling the Federal Government to command such available information as was essential for wise action, a central bureau for planning and statistics was organized and, at the height of the need, operated for several months. But as soon as the need began to diminish this admirable idea and its initial expression were abandoned. Thus was once more exemplified the general inability to appreciate the importance of providing organization and apparatus to make human knowledge readily available.

In the Army and the Navy, intelligence services, with the advent of war, emerged from dark corners and spread knowledge-seeking tentacles throughout the world. Rapidly these military bureaus evolved systems of gathering, classifying, and distributing information of essential importance to a nation at war. For a time the military departments were immersed in positive and negative intelligence, much of which doubtless was generally available to enemies as well as allies. Probably it will require years for these protective and defensive intelligence services to sink again into that oblivion which ignorance of world conditions tends to encourage. Seemingly, the more ignorant a nation, the safer it feels; and certainly the more ignorant an individual the less he appreciates the possible values of knowledge and of instrumentalities for commanding it.

NATIONAL RESEARCH COUNCIL—Last, because it is first in our interest as investigators, mention may be made of the informational work of the National Research Council. This was begun while the Council served as the Department of Science and Research of the National Council for Defense. At first there was organized a Research Information Committee with headquarters in Washington, and offices in London, Paris, and Rome. The principal and important function of this committee was to gather information about current research of military significance and to distribute reports of such work to appropriate military and civilian agencies. The committee served, through its staff of scientific directors or attachés, primarily as an information gathering and disseminating agency. Its success led to subsequent reorganization as the Research Information Service, concerning which more will be said later.

The various informational activities which have been selected as examples of types are all of them indicative of the need and opportunity which, compelling during the Great War, are always with us and are far more worthy of serious study and effort than is generally realized.

The World Situation

It has already been hinted that there was rare appreciation of the importance of human knowledge during the war and that we already are tending to lose this appreciation. With this observation in mind, it may prove worth while to make a hasty survey of the world situation.

GERMANY—Germany has the instrumentality for commanding scientific and technological information and for stimulation and guidance of research effort which all but gave her victory. This instrumentality, whose principal locus is Grosslichterfelde, includes the great national laboratories and the informational bureau which has quite naturally, but by no means accidentally, grown up in connection with "das königliche Materialprüfungsamt." The purpose of this institution, which was organized at Charlottenburg in 1871 and in 1904 moved to its present site, is to place at the service of the German people a staff of thoroughly competent specialists, armed with all technical facilities and records of human progress. This staff holds itself at the command of investigators, inventors, manufacturers, technologists, agriculturists, to assist in the solution of their practical problems and to help them to command the accumulated knowledge and progress of the whole world. This institution is said to have claimed to be able to answer 80 per cent of the problems put up to them supposedly demanding experimental research.

We may not reasonably flatter ourselves with the thought that we are exceptionally advanced in our consideration of informational needs and opportunities, for the chances are that in Germany, Japan, and probably other countries as well, plans have already been formulated, and possibly are well advanced toward practical expression, for the effective command of world informational resources in the interest of national development and prosperity. But whatever we do toward improving our informational resources, we can least of all afford to forget that as a nation we are backward in supporting, dignifying, and so far recognizing the values of constructive work that it necessarily commands the respect, attention, and confidence of our people, and is regarded as essential to human progress.

Yet, Germany does not stand alone in appreciation of informational need or in determined effort to meet it. England, years ago, was chief mover and responsible agency in the organization of the International Catalog of Scientific Literature, an ambitious project which ultimately failed because it was modeled too closely after the librarian's ideal of an index to knowledge. The Catalog, although undeniably useful as a list of all scientific publications, did not prove satisfactory to investigators and consequently failed to command their support. Its fate points a lesson which it is hoped we may heed, namely, that a mere catalog of titles is an entirely inadequate key to human knowledge. It demands supplementation, transformation, or both.

BELGIUM—Belgium also has witnessed an attempt to list and partly to summarize all published documents. In effect, this amounts to the construction of a classified card catalog to which one might turn with reasonable expectation of getting useful references or suggestions concerning almost any topic of human interest. This project also has suffered the ills of war and is moribund. We well may ask whether the plan was wisely conceived and whether, however thoroughly it may be carried out, it can reasonably be expected to meet our principal informational needs.

As has already been indicated, America, although full of informational agencies—industrial, scientific, political—has no general informational clearing house for all interests. Special informational bureaus or intelligence services come and go so rapidly that a directory cannot be kept to date. Washington is crowded with invaluable sources of information covering the entire range of human interests and activities. There are scores of federal offices, bureaus, divisions, departments which command useful information; but there is no individual and no bureau which serves as guide or directory. Consequently, the search for information in the great national center of intelligence is likely to prove baffling, discouraging, and, at worst, irritating. What could readily be done for informational Washington by the creation of a central clearing house, what indeed already has been attempted for quite another purpose by the Bureau of Efficiency, certainly should be done at once and with the greatest human foresight and skill for our entire country, for the world, because the isolated or independent nation is a fiction, and for the whole of human knowledge, historical as well as current. Nowhere in the world, so far as present information indicates, is there in plan or operation an informational clearing house conceived on a large scale with intent to render the whole range of human information increasingly accessible and useful. It is precisely such an informational organization that our times, our industries, our investigators, our public institutions, our public servants, and our people need. The realization of need in most quarters is not yet compelling, but in others it is definitely sensed and it is believed that the time is ripe boldly to extend the plans of the Research Information Service of the National Research Council.


W. W. Skinner


Charles L. Parsons

Research Information Service, National Research Council

From the Research Council's committee on research information, following the Armistice, was organized a division of the permanent Council called the "Research Information Service." It was my pleasure and responsibility to assist in planning, organizing, and furthering this informational agency. The Service has now been available for three years. During the first two years attention was centered on the study of the informational situation, the formulation of plans, and the creation of fundamental informational tools. From three years of effort to discover, understand, and satisfy informational demands, certain principles of organization and policy have appeared. These have been carefully considered by an organizing committee which is representative of research interests and of the principal industries and types of informational agency of the country. Foremost among the principles agreed upon by this committee on organization are the following:

1—The desirability of developing initially a general clearing house for scientific and technological information rather than a mere storehouse or depository of knowledge.

2—The conduct of a free informational service for the promotion of research, useful applications of its results and the supplying or disseminating of knowledge necessary for or beneficial to human welfare and progress. It is recognized by the committee that there is a practical limit to the possibility of free service beyond which charge sufficient to cover the cost of service should be made.

3—The encouragement and fostering of a miscellaneous request service initially limited to scientific and technological knowledge which shall strive to supply reliable information concerning any aspect or relations of research. Especially to be mentioned in this connection is information concerning research problems, projects, methods, processes, results, current work, laboratories, equipment, apparatus, funds, and other means of support, persons engaged in constructive or creative work, publications, and bibliographies.

4—The primary task of the special staff of the Research Information Service is set forth as the designing and construction of informational keys, instruments or tools essential to the efficient functioning of a clearing house for human knowledge. The final purpose in endeavoring to create informational instruments is the development of a complete coördinated machinery for gathering, classifying, locating when needed, and disseminating trustworthy information.

5—Utilization by the Service of correspondence, informational publications, and publicity as ways of meeting the informational needs of organizations and individuals, and of educating the public to appreciation of the possible values of a carefully planned and efficiently conducted informational clearing house.

The group of men, among whom appear several of our chemical colleagues, which has been chiefly responsible for the launching and development of this project naturally has come to look upon it as America's most ambitious, most thoughtful, and most promising attempt to be useful in a large way and permanently in connection with the handling of the varied and multitudinous products of human thought and ingenuity. Dr. James R. Angell, first chairman of the post bellum Research Council, once characterized the painstaking, albeit somewhat discouraging, labors of the Research Information Service Committee as primarily an "investment in brains." He believed firmly in the wisdom of this investment and in the supreme importance of the Council's informational opportunity.

To repeat, even casual observation serves to indicate the scattered and special character of sources of knowledge and the extreme improbability that a needy individual will happen upon the right source. It is only by happy accident that one locates satisfactory information outside the field of his special interest and activity. There is neither correlation nor coördination; there is not even a central medium of communication to place those who desire information in touch with those who have it. It is proposed, therefore, to make the Research Information Service of the National Research Council a great clearing house for informational requests and thus to increase the availability and value of existing sources and to supplement them as necessary. The Service will not strive for encyclopedic knowledge, save of sources, but undoubtedly its files will gradually acquire value. Ultimately it may become a great informational center, as well as clearing house.


Edward Bartow


Percy H. Walker

Although at present the Service is rather strictly limiting its activities to the natural sciences and their practical applications in industry and engineering, it is proposed to direct its development along those lines which promise to promote both increase of human knowledge through constructive effort and improved availability of knowledge already achieved. Once suitable clearing-house machinery has been designed, constructed, and perfected, there is no obvious reason why the plan which has been outlined should not be applied to the entirety of human knowledge.

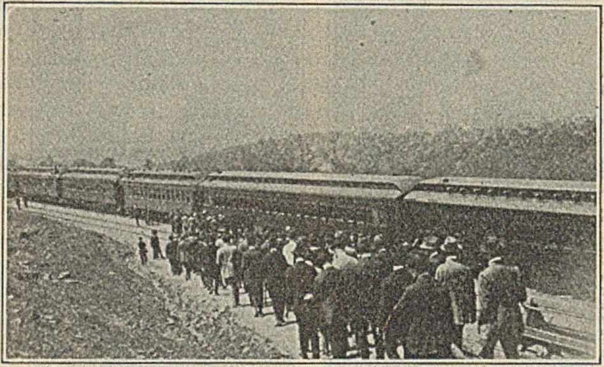
Although it is commonly believed that the important products of human skill and labor are satisfactorily transmitted from generation to generation it is important to note that this is not true of those products of mental labor which gain expression merely in written language. Useful inventions, commercially developed, are not likely to be lost except by replacement, but verbal descriptions of discoveries or inventions which have not achieved material expression are very likely to become buried in our great informational storehouse, our libraries. In the light of this condition, it has seemed peculiarly important to develop an informational service to supplement the library. This evidently means new types of keys to knowledge. The staff of the Information Service has planned and begun to develop files for research personnel, problems, results, laboratories, methods, procedures, experimental equipment, and bibliographies. It is surprisingly easy in this kind of venture to design special equipment which cannot be operated successfully because of its needless complexity, size, or costliness. The tendency is always toward specialization and against the creation of efficient clearing-house machinery.

It is now pretty generally recognized that the first and most important step toward increased availability of information should be the preparation of reliable objective, analytical abstracts of literature, and the construction of detailed subject indexes. If the scientific and technological literature of the world were regularly and systematically abstracted and listed, and if all this condensed information were available in the Research Information Service, it is reasonable to anticipate that from 70 to 90 per cent of all requests could be answered directly and with reasonable satisfactoriness from this single master-key. Were this proposed key to published materials supplemented by files of records concerning current research, scientific and technological workers, laboratories—their construction, equipment, etc., it is certain that many more requests could be successfully answered.

The Service has undertaken to develop, as its fundamental tools, first, a list of informational sources including individuals as well as organizations, specialists as well as informational bureaus; second, it is building up a library of source books which it is hoped may ultimately become an invaluable master-key to published information. Scarcely less important than these two types of key for clearing house use is the research personnel file which is counted upon to supply reliable information concerning all research workers, their resources for research, their interests, and their principal lines of activity. This file already contains nearly 14,000 names and is being mechanized by the use of the Findex system for convenience and accuracy of sorting. It is cited merely as an example of a type of master-key which, if skilfully planned and efficiently developed, an informational clearing house is sure to find entirely essential and of steadily increasing value.

As is true in many other directions, the best way to appreciate the problems of an information service, its need, and the value of devices for meeting them, is to try to use the Service and to follow as closely as may be the functioning of the clearing-house mechanisms in supplying information.

American chemists are far better situated informationally than are most other groups of scientists or technologists. Similarly, the chemical industries have been conspicuously more progressive in their efforts to command scientific and technological information than have other commercial interests. To what extent this is due to the necessity created by German initiative and resourcefulness is difficult to determine, but certainly the German influence has been considerable. And with all its provisions for marshaling and promptly commanding pertinent information, it is clear that American chemistry is not in the strongest possible position and that it still must reckon with species of ignorance and forms of competition which are as inimical to national welfare as they are to professional progress. It is entirely fair to ask, "Would not systematic, sustained, intelligent study of informational needs and values be likely to result in great improvement for chemistry?" My own observations and experience in connection with our Chemical Intelligence Department indicate an affirmative reply.



Getting on Train after Visit to Ishkooda Iron Mine, on Industrial Excursion

Chemistry and chemists, as well as those who as laymen seek chemical information, undoubtedly can profit greatly by a wisely planned and efficiently conducted general informational clearing house. We especially need such a service to facilitate contacts with related fields of research and with discoveries, inventions, and developments which, although not chemical, have significance for our special interests. We need such a general clearing house also to increase our profitable contacts with the consuming public. We need it to supplement our own keys to chemical literature, our abstracts, indexes, compilations of information, and even our special informational agencies, such as the Chemical Catalog Company, for through the sort of national informational clearing house which the Research Council is undertaking to create our special informational aids in chemistry will be made available to untold millions of scientists, industrialists, and consumers of chemical products.

It is greatly to be desired that ultimately an international service of this character be established with not a single locus, but with branches in most of the important countries, containing on file in each all of the material collected, so that in case of a cataclysm such as has befallen Russia and which might have befallen all of Europe if the World War had lasted much longer, it would not result in the loss to the world of a large part of her wealth of information. Such an arrangement if it were possible would require governmental coöperation but would result in a tremendous saving of effort and be all-embracing.

The Research Information Service of the National Research Council is a public service agency. It is ours to make or to mar, to use or neglect. It urgently invites our coöperation and freely offers its aid to us individually and collectively. We cannot afford to do less than interest ourselves intelligently in this difficult undertaking whose possibilities of usefulness are almost limitless and to endeavor to aid in so directing its further development that it may command our support increasingly.

Before closing I wish to call attention to the valuable results already accomplished by the Research Information Service of the National Research Council, due to the untiring and invaluable efforts of Chairman Robert M. Yerkes, at whose suggestion this paper was prepared.

Recent Developments in the Chemistry of Rubber

By William C. Geer

Vice President, The B. F. Goodrich Company, Akron, Ohio

RUBBER as it appears to the consumer in the form of tires, hose, or rubber overshoes is not a chemical individual derived by the operation of chemical processes nor is it the crude rubber of nature. The rubber articles are made up from one or more of thousands of mixtures, each composed of several different substances. These substances are made into mixtures by mechanical means, and to give them the physical properties required each must be submitted to the one chemical process of the industry, the action of temperature and time known as vulcanization. To attain highest values, the chemistry of these raw materials, of the vulcanization operation, and of the finished mixtures has been diligently studied during the past few years. From this study have come some interesting developments.

Early Development

While rubber was made known in its raw or crude form to the Europeans by Columbus, and other explorers in the sixteenth century, it remained until the third decade of the nineteenth century for a phase of its chemistry to be recognized in a practical way, and only within the past few years have chemists come to reasonable conclusions with respect to the mechanism even of this fundamental reaction. You may pardon me, therefore, if I refresh your memory with some of the older and to rubber men, well-known ideas, in order to pave the way for a brief discussion of the new.

The raw rubber is a vegetable product derived from the milk or latex which flows after cutting the bark of certain trees which grow profusely in a belt about two hundred and fifty miles each side of the equator in countries where the soil, rainfall, and climate are propitious. Spaniards in the sixteenth century saw South American natives spread this latex upon crude fabric. The crude rubber layer thus formed served as an excellent waterproofing medium. The first rubber shoes were made by the Indians, who poured latex over clay lasts and dried it in the smoke of a fire. Men, like cats, abhor wet feet, and shoes are really our earliest useful application of rubber.

The dried product, as a brown, frequently evil-smelling body, came into Europe in the eighteenth century. From then on, chemists and practical men studied this product in the attempt not only to determine its composition but also to find ways and means of utilizing it. Priestley named it, Faraday analyzed it, Hancock found uses for it, but there were fundamental difficulties which restricted its use and caused many thousands of articles to be returned to the manufacturers. The rubber was found to "dissolve," as it was termed, in turpentine and coal-tar naphtha. This solution or cement was spread upon cloth to make raincoats. It had, however, the disadvantage of being sticky and of softening with heat and stiffening with cold. Even the milder climate of England, but especially the heat of our American summers, caused the coats to fall apart and to stiffen so decidedly when worn in the winter that they became virtually like tin armor. An early story has been told of a man who wore one of these coats in the winter in New York, who, finding the garment so stiff that it was difficult for him to get around with it on, came in and sat down in front of a hot fire in order to soften it. It did soften and too much so, for it became necessary for friends literally to cut the garment from him. Investigators with scientific as well as only inventive training made efforts to dry and stiffen the product, and this led to the development of mixing machinery. The rubber mixture was thus developed.

One early practical man, Hayward, conceived the idea of dusting sulfur upon the surface of rubberized cloth and submitting it to the action of sunlight; he found a drying action on the surface but no change in the effect of heat and cold. One day a hardware merchant who had failed in business but who was of an inventive turn of mind, Charles Goodyear, was attracted to the window display of a rubber company in New York, where he saw life preservers made of rubberized fabric. One thing led to another, and he was stimulated, as he says in his memoirs, to study means for eliminating the undesirable effects of temperature. He learned of the Hayward patent, purchased it, and began experiments with the mixing of sulfur into this crude rubber. Finally, to tell his own story, he observed one day in January 1839 that certain mail bags which had been returned by the Government, the rubber part of which consisted of a mixture of rubber, sulfur, and white lead, had not softened after standing for some time in the vicinity of a hot stove. Without scientific training, but with the instincts of an investigator, he at once was led to further experiment as a result of this observation. He made numerous trials until he came clearly to the conclusion that time and temperature with a rubber-sulfur mixture were the two controllable factors which would cause a change in rubber by which it would remain flexible in the cold and not melt when heated. This process was later named vulcanization. Vulcanization, however, changed not alone the hardness under changing temperature conditions but altered a number of other physical properties. The breaking or tensile strength, which is a most important property for industrial and service uses, was increased.

William C. Geer

I have mentioned this incident in the history of rubber, purely to give credit to those early scientific minds, for we all know how many of the greatest discoveries in the laboratories of the scientists, in the practical work of the factories or even in the crude workshop of an untrained inventor, are due to keenness of observation. If young men under training or who are at work in our factory laboratories could only learn that at least one fundamental for success is the faculty of keen observation to see leads into new territory, how much faster would our research work proceed! Goodyear not only discovered the fact of an interaction between rubber and sulfur, but he also discovered and described in his patent the first accelerator of vulcanization, the Dutch process white lead.

The growth of the rubber industry from its meager output of $7,000,000 worth of products in 1850 to $1,122,000,000 worth in 1919, all of this being based upon this fundamental principle, is one of our striking industrial achievements. These facts of early history show how close should be the connection between mechanical invention and chemical research. Chemists are quite justified in using the term "research" for their part of such coördinate enterprise. The inventions of the early workers failed to develop the rubber industry. I think we must call Goodyear a chemist, although he was not trained as such; but sometimes men become chemists or physicists, or even financiers, without training.

CRUDE RUBBER

Let us go back now and trace step by step rubber as it grows in the tree down to its use in practical products and discuss some of the recent developments which give us a deeper insight into the chemistry of these various processes. Through the researches of DeVries and others our knowledge of the chemistry of the latex and of raw rubber has come to scientific exactness. Rubber latex is a colloidal suspension. It exhibits the Brownian movement, and under the microscope the size of the particle is approximately 0.0005 to 0.003 millimeter. These globules are not always spherical. Since it has characteristics of a solid it is reasonable to suppose that crude rubber is produced in the tree in glands or cells which put it into the watery fluid or serum of the latex in solid form.

An average analysis of the latex shows it to contain the rubber hydrocarbon as its chief constituent to the extent of 28 per cent, 1 to 3 per cent of resins, mineral matter, sugars of several kinds about which little is known, proteins, if we may call the nitrogenous matter by this general name; the balance, about 60 per cent, is water. Commercial rubber includes several of these substances and so exists to about 30 to 35 per cent in the latex. It is highly probable, in view of the action of different grades of commercial rubber, that the resins are in solution in the rubber hydrocarbon; it is pretty definitely known that the protein plays the part of a protective colloid. There is an interesting field for colloid study here, for the protective action of these proteins in the latex is different in different species of trees. That from the Hevea tree does not cream on standing nor can these fine particles be separated by any centrifuging process that has yet been applied to it. On the other hand, the latex from other trees, notably the Castilloa, will cream with relative ease, and rubber may be separated by mechanical means. We may possibly compare the percentages which have been given with that of milk in which the butter fat runs only from 3 to 6 per cent, and the proteins from 3 to 4 per cent, and which readily creams on standing.

Rubber latex, the moment it comes from the tree, begins to change; the action of bacteria is rapid, probably first affecting the proteins, changing them to amino acids, amines, and various other decomposition products. It is highly important in the practical handling of latex to carry it to its first manufacturing step before these bacteria can make too great an alteration in this liquid; otherwise crude rubber of different colors and physical properties would result with consequent lessening of its value in the markets.

COAGULATION—The first step in the manufacture of crude rubber consists in coagulation, around the study of which there has been a great deal of scientific work. Investigators have found, as those who understand colloid chemistry would expect, that dilution of the latex to a standard rubber concentration is the first fundamental, and the second one is the breaking down of the protective action of colloids by means of acid of the right concentration. Various acids have been tried: formic, sulfuric, hydrochloric, and others. Various electrolytes have been used, but up to the present time a concentration of about 1 per cent (in terms of rubber) of acetic acid gives the best product.

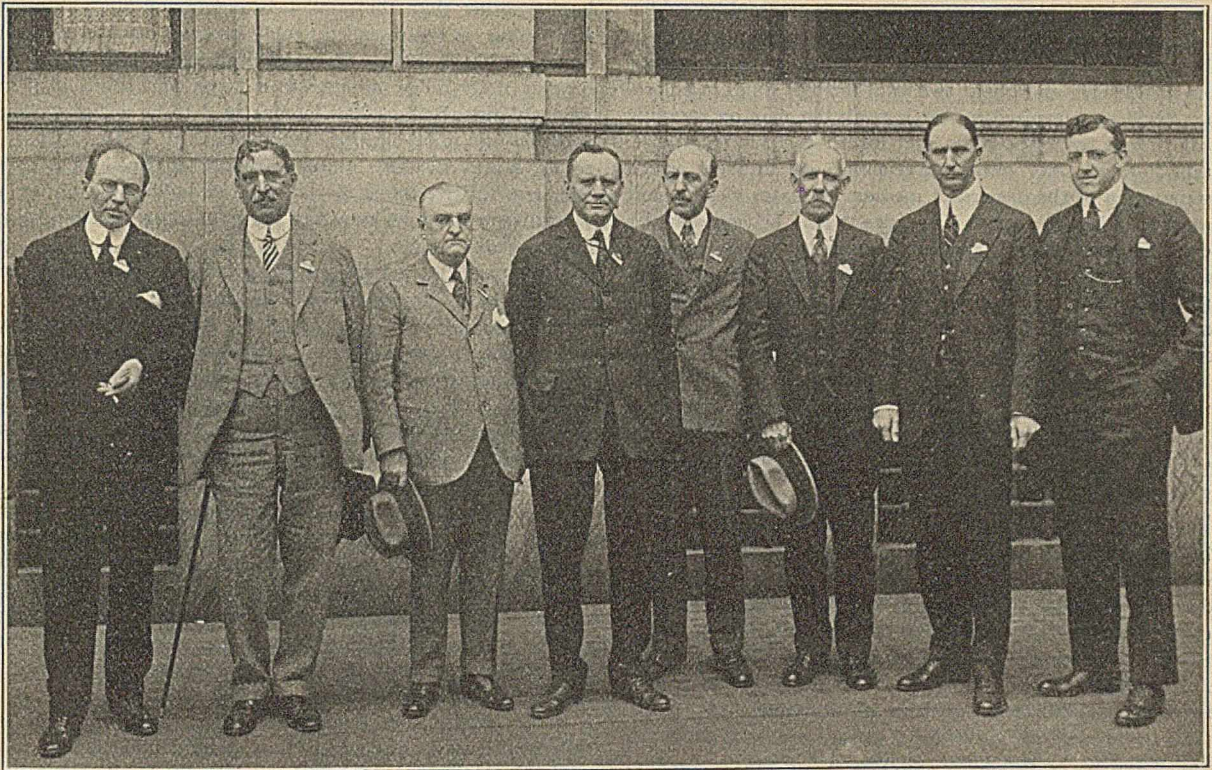
Coagulation is known to be a simple massing together of the rubber globules. The rubber itself is not changed, and as a result of this addition there is formed at first a soft, white dough which, when congealed enough to be capable of practical handling, is washed free from serum, acid, and other substances upon a washing mill. About 95 per cent of the rubber now prepared on the estates is made by the acetic acid method, which gives a crude material of good appearance. When made in this way and where discoloration is prevented by small quantities of sodium bisulfite, there results the "pale crepe" of commerce. When, however, the sodium bisulfite is not used, and in addition an attempt is made to imitate the smoky odor and appearance of the original Brazilian grade by a smokehouse process applied after the rubber has been washed and partially dried, there result the "smoked sheets" of commerce.

There are many unsolved problems of a mechanical as well as of a chemical character. A most excellent grade of crude rubber has come into the market in recent years which is prepared by the total evaporation of the latex. This has good properties, although not greatly different from that prepared by the method already briefly described. The real field here probably lies in a study of the action of polymerizing chemicals, for there is no better place to submit a substance to chemical action than when it is in its most finely divided state. Some day enterprising chemists, either of the rubber factories or in connection with the government experiment stations or private estates, will study substances to be added to the latex to serve as polymerization agents prior to coagulation to give us grades still better than we now receive.

CULTIVATION—The cultivation of rubber trees on plantations or estates is the result of an idea of the Englishman, Hancock, who suggested it in 1856. It was carried to completion by another Englishman, Sir Henry Wickham, who in 1876, with the support of the officials of the Kew Botanical Gardens, succeeded in shipping out of South America some seeds of the best tree, the black *Hevea brasiliensis.* The seeds were planted in the Kew Botanical Gardens. The young sprouts were sent to Ceylon; seeds from these trees were sent in later years to Sumatra and the Malay Peninsula. From then on, the rubber plantation industry has grown, and it only remained for the tremendous demand incident to the use of crude rubber to support the automobiles of the world, until an industry which produced but four tons in 1900 developed a production of 304,000 tons in 1920. Over seventy-five per cent of the total world's product comes to America. To supply the world with 300,000 tons of crude rubber requires about 270,000,000 gallons of rubber milk. Of these tons which come into America, about 75 per cent are used in pneumatic tires, solid tires, and inner tubes. Probably one-third to one-half of the world's production comes to the city of Akron, Ohio.

There were under cultivation only 116,000 acres in 1905 and over 3,000,000 acres in 1920; over 70 per cent of this acreage is owned by British capital and about 66 per cent of it is under the political control of Great Britain in her Colonies. As a result of the tremendous demand in 1910 and the over-supply in 1920, the price of this material fell from $3.00 a pound to about 13 cents a pound. When one considers that the cost of production of plantation rubber varies from 18 to 25 cents per pound, it is obvious that additional ideas for its use in new articles will be most welcome. In the economics of rubber illustrated by these figures, London is to-day the financial center, the city of Singapore on the Malay Peninsula the shipping center, and Akron the manufacturing center.

COMPOSITION—This plastic raw rubber is shown by the best analyses to consist of the rubber hydrocarbon 92 to 94 per cent, 1 to 4 per cent of moisture, mineral matter, resins, and proteins; in other words it is not far from the composition of the latex, with the exception of water and water-soluble ingredients. Ultimate analysis shows the composition of the rubber hydrocarbon to be $(C_5H_8)_x$. On account of the supposed relation of rubber to the true terpenes, we customarily think of it in terms of the formula $(C_{10}H_{16})_{x/2}$. The structure of the hydrocarbon has been subjected to much controversy. Chemists now generally agree. Isoprene, C_5H_8, is a methyl derivative of butadiene. This butadiene hydrocarbon consists of a chain of four carbon atoms with alternate double bonds, or a conjugated system of double bonds. Addition to such a system takes place at the ends and causes the formation of a double bond in the center. We believe that the polymerization of isoprene to rubber consists in the addition of one molecule to another in



W. Lee Lewis, Charles L. Reese, Van H. Manning, John E. Teeple, William McPherson, Francis P. Venable, Martin H. Ittner, B. R. Tunison

this way, forming a succession of these groups linked together into a ring of uncertain dimensions. How far the chemical composition or state of polymerization, or the state of aggregation of the polymerized magmas affect the properties of crude rubber as we know them, and how far the hydrocarbon from trees of various ages differs chemically and physically are all unknown phases of this interesting problem. We do not know the part played by mineral substances nor the exact condition of the nitrogenous matter, although the proteins have a most important influence upon the colloid characteristics of the rubber.

Much study has been made by some chemists in the analysis of rubber to determine the percentage of acetone-soluble matter. Rubber from different botanical species varies largely in resins. Vulcanized rubber changes on standing, owing to the formation of acetone-soluble oxidization products. The rubber resins are highly complex and whether they were the original source of rubber in the tree or whether they have been produced from the rubber we do not know. The acetone extract is probably to-day the one reasonably reliable means of determining the botanical origin of different grades, and the fresh from the deteriorated rubber, although the control of quality in a finished article can be carried on irrespective of the origin of the rubber, and the amount of acetone extract is not, as some have believed, a guide to quality of a vulcanized rubber mixture.

The chief chemical property of the rubber hydrocarbon is unsaturation. It adds directly halogens, halogen acids, sulfur, and sulfur chloride, as well as certain other substances.

The story of synthetic rubber has been much discussed. Synthesis of it is a well-known fact. Much work was done upon it during the war, in Germany, where considerable quantities were produced, but it was not the same hydrocarbon as that derived from the tree. It was a close relative known as methyl rubber. However, the tires and other soft rubber articles made from it were decidedly inferior in service. It was, however, valuable in hard rubber or ebonite.

Colloid Chemistry

The study of the colloid characteristics of raw rubber constitute an important field in which our knowledge is growing. Consider that the latex contains innumerable very small solid particles surrounded by a protective colloid. On massing the rubber together there is reason to believe that a definite structure remains. The rubber is probably still surrounded by the film of protective protein colloid, or in any event the interfacial tension between these particles when massed remains great enough to have an appreciable effect upon the properties of the substance. When rubber is softened, or as we call it masticated, upon a mixing mill, even with the minimum of heat, a change occurs, in which probably the protective colloid is broken up and mixed with the rubber, without, however, radically altering its vulcanization properties. A cement of softened or masticated rubber in benzene is thinner than one made of unworked crude rubber. This phenomenon could lead one to believe that this crude rubber may contain a structure which can be broken down by mechanical action but not by the method of absorption in a solvent. When a sufficient amount of it is placed in a solvent it swells, showing absorption of the solvent by the rubber, and only after a long period of time will it become a viscous solution or cement. Indeed to gain uniformity it is necessary to beat it up. Yet in this form it is not a gel and does not show the phenomenon of syneresis. These data seem to indicate that a benzene rubber cement is therefore simply an emulsion of benzene dissolved in rubber as one component, dispersed in benzene as the other component.

Some interesting studies by Stevens in England on vulcanization in solutions are presenting some leads into the colloid chemistry which if followed may give us information of marked value. It has long been known that when vulcanized rubber is placed in solvents it does not dissolve but merely swells, the swelling action being one and one-half times in ethyl ether, nearly double in benzene, and about two and one-half times in chloroform. Swollen vulcanized rubber is weak but may on standing lose the liquid by evaporation and return to its original size. Stevens, however, has vulcanized a rubber sol to a gel, which on evaporation of the dispersion medium he states yields a soft vulcanized rubber of normal properties. This he has done by the cold or sulfur chloride vulcanization method, working with benzene solutions of masticated plantation rubber. He has formed gels almost immediately. Syneresis sets in and the gel contracts, expelling the solvent which contains little or no dissolved rubber. He has also obtained vulcanized rubber sols by heating raw rubber sols in a sealed vessel under pressure. These on spontaneous evaporation yield films of vulcanized rubber which cannot be redissolved in rubber solvents. There is much of interest to be determined from a pursuit of this field.

Absorption of Light

The absorption of light by crude rubber has recently been investigated by Lewis and Porritt, who find no decisive evidence of absorption bands, but a general absorption which is fairly strong for wave lengths below 2700 but rapidly diminishes with increase in wave length. It may be that this investigation will give us further evidence and an explanation of why the rubber is so rapidly oxidized in the presence of ultraviolet light.

Diffusion of Gases

The early studies of crude rubber with respect to diffusion of gases through it have recently been worked out on a scientific basis for both crude and vulcanized rubber by Venable and Fuwa, who examined two grades of crude rubber and two vulcanized compositions. This work was stimulated by the use of rubberized balloon fabric during the war, and these investigators made a most interesting and valuable contribution in relation to balloon work. The amount of gas thus held in the rubber was directly proportional to the pressure, and unaffected by the degree of vulcanization or the presence of compounding ingredients. They verified the customary assumption that the mechanism by which a gas penetrates a rubber membrane is through diffusion of the gas, which is held in true solution. This, it is to be hoped, will lead to a further investigation so far as hydrogen and helium penetration are concerned, to find components which will reduce the solubility of these gases in rubber mixtures. Could we use in dirigible balloons a rubber mixture highly insoluble toward hydrogen and helium a great advance could be made.

Another problem in this field is the development of a rubber mixture in which war poison gases are insoluble. Our Washington friends may agree to abolish poison gases from warfare. We should, however, be active in preparation of methods of defense against it. We are forbidden to carry concealed weapons, but there is no law of God or man to prevent us from the use of locks on our doors and bolts on our windows.

I would earnestly recommend to the American Chemical Society the extension of gas defense research to investigate gas mask and other protective clothing, alone as far-sighted patriotic citizens if coöperation with the War Department be not allowed. It is a field in which research work of a coöperative character can be undertaken, with who knows what valuable results to us in the future.

Vulcanization

The chemistry of vulcanization is probably that phase of rubber chemistry which has attracted the most attention during recent years. One of the earliest of the various processes of vulcanization, other than the previously mentioned hot vulcanization with sulfur, is the so-called "cold" process, discovered by Alexander Parkes in 1846. He vulcanized sheeted crude rubber by dipping it for a few minutes in a 1 per cent solution of sulfur monochloride, S_2Cl_2. This is conceived to be a direct chemical addition up to a limiting composition of $C_{10}H_{16}.S_2Cl_2$. This result, however, yields a solid, usually obtained as a powder. When quantities under 3 per cent are added we obtain soft, vulcanized rubber, as known in the form of toy balloons, nipples, and surgeons' gloves.

THE PEACHEY PROCESS—A most interesting cold process has recently been developed by the Englishman, Peachey, who first proposed his new plan in 1918. This new process consists in exposing rubber alone, or a mixture containing any useful pigment, to two gases alternately, namely, sulfur dioxide and hydrogen sulfide. The first diffuses into the rubber until the proper quantity has been taken up and then the second gas is permitted to diffuse in it. They interact with the liberation of nascent sulfur, bringing about a rapid vulcanization without the aid of heat. The claims made for the process consist essentially in the advantage given to rubber compositions which would otherwise be injured if the usual hot vulcanization method is employed. Mixtures containing leather, cotton fiber, and colors which would be altered by heat, particularly with respect to rubber surface clothing, may now be vulcanized at ordinary temperatures without injury. The process has not yet been conducted on a large production scale.

NITRO COMPOUNDS—Somewhat earlier, in 1915, the Russian, Ostromuislenskii, discovered that a hardening similar to vulcanization occurred when rubber is heated without sulfur in the presence of certain nitro compounds or peroxides, such as trinitrobenzene or benzoyl peroxide. Whether this is a gelation phenomenon, an adsorption, or an additive chemical reaction has as yet not been proved.

HOT VULCANIZATION—We now come to a discussion of what has been learned regarding the hot vulcanization of rubber with sulfur, which is the only process in large commercial use. The idea prevalent fifteen years ago when I first entered the rubber industry, and one which still prevails in the minds of many practical men, is that sulfur vulcanization does not occur until the temperature of the mixture has reached or exceeded the melting point of sulfur. Vulcanization to-day, however, is known to occur at ordinary temperatures if the time be long enough—sixty to ninety days in the case of old-fashioned mixtures. When certain recently discovered powerful catalysts are employed in the mixture, the hardening may take place on standing over night. Whether the temperature be low or high, we know that the amount of sulfur that enters into combination with rubber increases with time and rise of temperature; that is, the velocity of the reaction is proportional to the time at constant temperature and if the temperature and the time be fixed, the amount of sulfur entering into the molecule is dependent upon the quantity originally present.

When small amounts of, say, 3 per cent of sulfur are thus "combined," as we say, there results the soft rubber of commerce. In almost all instances there is a slight excess of sulfur left in solution in the rubber as "free" sulfur. This usually gradually diffuses to the surface, where it crystallizes out and appears as a powder or "bloom." This amount of combined sulfur, expressed as a percentage figure in terms of rubber as 100 per cent, is known as the "coefficient of vulcanization." No chemical individual of the rubber hydrocarbon and sulfur has been isolated from soft, vulcanized rubber mixtures. Yet their properties vary from the under-vulcanized, or "under-cured," mixtures in which the amount of combined sulfur is low, to the over-vulcanized, or "over-cured," mixtures in which the amount is high.

There are wide and, to the manufacturer and consumer, vitally important differences in physical properties, between under-, proper, and over-cured rubber articles. Yet we have as yet only theories of a general character to explain the nature of the product of vulcanization.

When a large excess of sulfur is used in a mixture, addition goes on up to a maximum of 32 per cent of combined sulfur, and there results the only compound which has been isolated—a monosulfide, C_5H_8S, or, as usually written, $C_{10}H_{16}S_2$. It is in the laboratory a brown, dry powder. In the factory and in commerce we know it as hard rubber or ebonite, in battery jars, sheets, fountain pens, and so on.

Ostwald's theory of physical change led to the many discussions that have arisen between the two camps of chemists: those who expound the sulfur adsorption theory of Ostwald and those who stand by a chemical theory. The great father of rubber chemistry, Weber, was an exponent of the chemical theory. We to-day, I believe, adhere to a combination of a chemical and physical theory as most reasonable for the explanation of vulcanization. The fact that no compounds have yet been isolated in the soft rubber range of vulcanization is no reason for us to believe that a purely physical theory alone will account for it.

We have not yet found a process by which the combined sulfur can be removed and the original rubber regenerated. The rubber industry is, however, economical, and uses up its waste products. The old tires, shoes, and hose are gathered and reclaimed by processes which simply hydrolyze and separate the cotton while the vulcanized rubber is softened to permit it to be plastic enough for remixing. Let me here state in justice to my brethren in the industry, all statements to the contrary notwithstanding, that reclaimed rubber is a valuable ingredient in many rubber mixtures. Over 70,000,000 pounds are used annually in this country, or about one-quarter of the amount of crude rubber employed; an economic consumption of no mean magnitude, of what otherwise would be waste.

ACCELERATORS

While the nature of the product obtained when sulfur and rubber interacts is indefinite, the rubber chemists in recent years have reached some pretty clear conceptions of the mechanism of the process, particularly the part played by catalysts. From the day when Goodyear used white lead, various types of inorganic compounds have been employed as accelerators. They have been chiefly lead compounds and oxides of the alkaline earths, with, in laboratory experimentation, for instance, the hydroxides of the alkali metals and the sulfides, and hydrosulfides of the alkalies and alkaline earths.

The use of organic compounds for speeding the time of vulcanization is probably one of the most important developments in the chemistry of rubber and of greatest value in practical affairs. They have served not only to increase the rapidity of turn-over in the factories, but have led to increased physical properties of rubber mixtures. The name of the first person to use organic accelerators in rubber factory practice has never been published. The writer feels it to be in the interests of truth to give here public credit to the two pioneers of the organic accelerator. The laboratory record books of The Diamond Rubber Company, which was later consolidated with The B. F. Goodrich Company, show that Mr. George Oenslager, in the early months of 1906, experimented with aniline oil, and a long list of other organic compounds, with the definite purpose of hastening the time of vulcanization. In June of that year, Mr. A. H. Marks directed its use in factory formulas, and in February 1907 he used thiocarbanilide. The German patents were not published in this country until 1912, so that it may be safely stated, unless some one comes forward with earlier unpublished data, that the use of the organic catalysts of vulcanization originated with Mr. Oenslager and Mr. Marks in 1906.

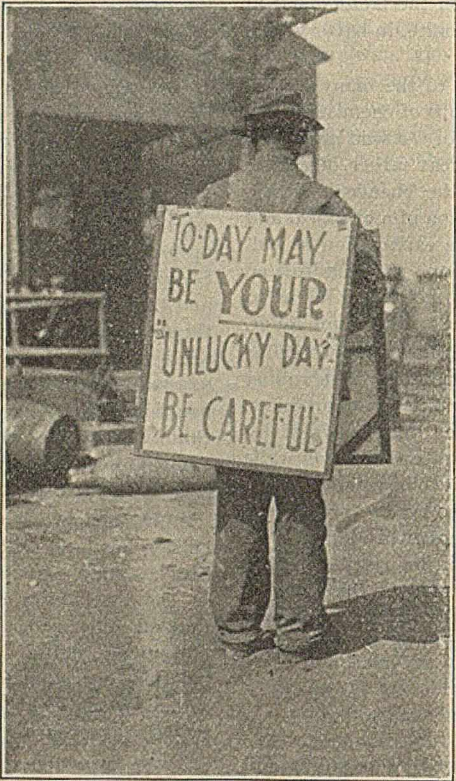
Basic compounds were first used, particularly nitrogen derivatives. The literature mentions large numbers of them; piperidine, aldehyde ammonia, hexamethylenetetramine, the aliphatic amines, and so on, have been used in practice. The dithiocarbamates came into published literature with Ostromuislenskii in 1915. Bruni, Maximoff, and others have studied the thiuram disulfides, and within the last few years the xanthates, particularly the zinc salts, have been discussed. In rubber mixtures, for laboratory purposes, accelerators have been found which permit the vulcanization of rubber and sulfur at all ordinary temperatures. Mixtures can now be made which will vulcanize over night on standing at room temperatures and at very short times from then on up to usual factory practice, which are temperatures under 150° C. By proper selection of accelerators, even cements may be vulcanized to gels on standing for several hours at room temperatures.

How these substances act and why, have been pretty well established. Zinc oxide in a mixture has long been known to promote the action of the accelerators. Kratz, Flower and Shapiro stated that zinc salts are formed in many instances, and that these are the active accelerators. They show how the thioureas can form zinc salts through tautomeric change. These are similar to the zinc dithiocarbamates. Bruni and Romani assume that the thiourea is converted into a zinc salt, as just mentioned, and that sulfur acting with this zinc salt forms a thiuram disulfide which acts as a vulcanizing agent. Twiss studied allotropic forms of sulfur but was able to show no difference in the action of the two.

In my opinion, however, the best work on the theory of acceleration has been that of Bedford and his associates, Sebrell and Scott. They show hydrogen sulfide to be an important factor in the mechanism of vulcanization and, generally speaking, that all vulcanizing reactions may be ascribed to some form of polysulfide sulfur. The original accelerator then, whether metallic, organo-metallic, or organic, forms with sulfur polysulfides which yield sulfur in a more active state than when in its elementary form.

These substances cannot be termed catalysts in the true sense, at least so far as our idea of contact catalysis is concerned. They do serve to permit sulfur to be more actively taken up by rubber, but in doing this they are often changed themselves and then are left permanently changed in the mixture. Intermediate compounds are formed. The reaction is more chemical than physical. There is no poisoning of the accelerator except the retarding action of acids. Nor is it a case where a given quantity may react with a relatively large amount of the reacting substances. The quantity of accelerator has a very definite relation to the time and degree of vulcanization. Furthermore, essentially all accelerators, according to the best of our evidence, such for instance as that of Whitby and Walker, show not only an increased speed of reaction but also an increase in the tensile properties of the rubber. We gain, therefore, two points: one, the velocity of reaction, and the other, improved physical properties. We had better call them accelerators and let it go at that.

The physical properties of rubber mixtures have been studied, and chemists are more and more coming to use the stress-strain relations as guides to the evaluation of mixtures. Wiegand, in a most interesting study, showed that the addition of different volumes of different dry inorganic powders which we call pigments increased the energy-absorbing capacity remarkably in the case of gas-black, lampblack, and zinc oxide; increased it to a slight degree in the case of a fine clay, but decreased it in the case of whiting, fossil flour, barytes, and glue. He also called attention to what the older rubber men have long known, that the tensile strength of a rubber mixture usually computed against the cross section when at rest and before testing may, if computed against the section at the break, exceed twenty tons per square inch, which would bring rubber into the class of mild steel. It is the only substance for which the elastic limit extends to the point of rupture. The number of foot-pounds of energy that can be stored in a unit weight of the material exceeds steel many times. It is an interesting physical study which tells us that such stored energy in tempered spring steel is only 95.3 foot-pounds, while in a high-grade rubber it is over 15,000 foot-pounds.



"Safety First" at Tennessee Coal, Iron & Railroad Company Plant

To explain the properties given to rubber mixtures by these dry powders, determinations have been made of the particle size, by Green and others, who have photographed under the microscope these various materials. From these and other data we come to one important conclusion, namely, that the particles of large size are not as strength-giving in rubber mixings as those of small, while particles which seem to separate from the rubber when stretched are the ones which are of less value in mixings which must resist abrasion.

The use of carbon black and zinc oxide is really based primarily not only on their fineness of subdivision, but on some factor which we have yet to determine but which may be due to an increase in the interfacial tension. That is, they are so fine in subdivision and so specific in their adhesion to rubber that they not only approximate what we may term "mass molecules" but have a degree of specific adhesion to the rubber, making it thereby difficult to break them loose when rubber is submitted to stress. There has been an amusing controversy between the exponents of the sale of carbon black and zinc oxide over which one is the best. I will leave it with you; they are the two best materials—one is the king and the other the queen of pigments. You may use them singly or together and take your choice as to which will have the preference in the processions of your royal family. Some unpublished data go to show, however, that both are essential to the highest values in some rubber mixtures.

You must not now let me leave you with the idea that these few substances constitute the whole of rubber mixtures. I wish they did, for then my early dream would approach realization. When I first came into the rubber industry fresh from a university I thought how easy it would be for me in a relatively short time to solve this compounding problem. I had been trained in the phase rule, with a reasonable amount of mass law and electrolytic dissociation thrown in for good measure, so I hoped, of course, to find rubber a simple three-component system capable of explanation on a triangular diagram. But as soon as I became acquainted with the properties in compounding of from 400 to 1500 dry pigments and with organic accelerators which in the years that have followed have run upwards of a thousand; with reclaimed rubber of a hundred grades; with crude rubber in twenty to a hundred different kinds, and all these to be used in mixtures with cotton fabric of thousands of weaves to make ten or twelve thousand different articles in different sizes, shapes, and for different purposes, I came to have a very high respect for the practical man. After all, rubber, as the consumer gets it, is not a simple mixture of rubber, sulfur, and accelerator; in the interests of numerous physical properties required for service in the form of shoes, frictions, treads, and belt covers, other materials must be used. We have found in recent years how these materials serve practical purposes and are not simply to be considered as cheapening fillers. In point of fact, to-day many pigments cost more than crude rubber. The colloid particle, the fumed products, and the ground inerts all have definite uses in giving us serviceable as well as economical rubber products. The rule-of-thumb methods are gone from the leading laboratories, but the variables are so extended that the service test has become the final judge of the value of any mixture.

May I be pardoned if I speak from the vantage of research and experience to those who would write specifications for rubber articles? For years plantation grown crude rubber was ruled out—organic accelerators and carbon black excluded. Yet the industry advanced, used these substances, and improved the quality of its products. Where specifications seem essential, may I recommend only tests, and those which have a definite relation to the service the article is to render?

While we have developed research laboratories to show us why, development departments to show us how, testing machinery to give us results, we, nevertheless, are constantly faced with the question: Will it age? Rubber is a perishable product. For any purpose a knowledge of the rate of deterioration is most advantageous. This is a serious problem and a vital one to manufacturer and consumer. Heat, light, oxygen, and sulfur play their parts in the drama but as yet no definite theory to account for the varied rate of aging has been proposed. In the vast majority of cases too rapid decay is due to over-cure of the mixture. To determine over-cure and how rapidly a new compound will age in comparison with one of known properties, I devised a test some ten years ago by which the rate of decay could be predicted. I have recently published some results from this ten years' experience from which I now believe that in the heat of 70° C. with plenty of air, one day in the "short life oven" corresponds to about six months of natural aging. I do not hesitate to recommend to my friends in the rubber industry more attention to this vital problem.

As not only a chemist but a practical rubber man, I could not let go this opportunity of saying something of the future of rubber. The automobile has made the rubber industry, just as the rubber industry has made the automobile. You could not enjoy your cars if you had to follow the practice of Germany during the war, with steel springs and wooden blocks and other devices which were used in the attempt to get along without the softness and springiness of the rubber tire. Improved highways, whether for train or motor car, are essential to human prosperity and growth. It is rubber in the form of tires, air brake hose, insulation, packing, and manifold others which has made these highways capable of efficient and comfortable use.

With about twelve million automobiles in the world and about ten million of them in the United States, one must look forward and let his mind revert from days of depression to the future of larger use of these articles. There are about twenty-four million homes in this country; there is scarcely a new house built nowadays without its garage. When one looks at the map of the world and considers the millions of people who will need improved highways for transportation purposes throughout the great continents of Asia and Africa, let alone an increasing desire for these facilities in Europe and America, we can expect a vast increase in motor car transportation and with it of rubber tires.

Rubber articles have woven their way into myriads of uses. We have found, for example, that soles and heels of rubber give comfort and yield long resistance to wear, for rubber mixtures outwear leather wherever they have been placed in comparison with it. The home, the shop, the school, the office, directly or indirectly, derive benefits from them. It is one of those substances which unfolds possibilities for new applications which stagger the imagination. The chemist has and will continue to play a most vital part in these developments. The automobile tire of ten years ago gave a satisfactory mileage of four thousand miles, while to-day the cord tire would scarcely be considered of value on your cars if it did not give you ten or more thousand miles. Essentially all rubber articles have been improved in service, achievements due in no small part to the developments in the chemistry of rubber of which I have spoken.

With this picture in mind, one can see only larger values, provided, I believe, that the chemists of this industry are supported by the financiers in the conduct of research work. Many problems are still unsolved; civilization changes; only as an industry bases its progress year by year upon the results of research, will it attain permanence in its growth.

Some Research Problems of the Canning Industry

By W. D. Bigelow

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In any branch of industrial research, problems must be studied which at first appear to have slight connection with the industry concerned. It is often necessary to investigate the character and methods of producing the raw materials. A study must be made of the purposes for which the finished products will be used, and the storage conditions to which they will be subjected.

The canning industry is no exception in this respect. The success of the industry depends first of all on the satisfaction and success of the growers who raise the raw products. The uniform quality of seed supplies is of fundamental importance. Serious consequences sometimes result from seed of low germinating power or of a different variety from that specified. The distribution of seed contaminated with fungus diseases is certain to cause disaster. The canner generally distributes seeds to his growers, directs them with respect to the time of harvesting, and in many ways is held responsible for the crops produced. He is therefore interested in a wide range of agricultural problems.

Again, after the food is manufactured and sold many questions arise regarding its transportation and storage. When shipped in the winter there is danger of freezing, which damages the appearance of some products. The amount of damage probably depends on several factors, including the extent of freezing, whether the product was stationary or being transported while freezing and thawing, and the time occupied in thawing. No systematic study has been made of the influence of freezing on the appearance and quality of canned foods.

Food Poisons

Questions sometimes arise regarding the wholesomeness of foods which have been consumed. Any sudden attack of illness involving abdominal distress is likely to be construed by consumers and sometimes by physicians as evidence of food poisoning, and some article of food recently consumed, and which the patient is not accustomed to eating, is sometimes designated as the probable cause of the illness. Thus it is important that our knowledge of the general subject of food poisoning be greatly extended.

The study of food poisoning is one that pertains peculiarly to public health, and it involves all classes of foods. There is no type of food poisoning that is peculiar to canned foods.

During the last generation our ideas of the character and cause of food poisoning have undergone a fundamental change. A generation ago a type of illness characterized by purging, vomiting, and great intestinal pain was known as ptomaine poisoning, and was believed to be caused by chemical products due to the splitting of the protein molecule by bacteria of unknown nature. Something more than twenty years ago it was shown in Europe that illness of this type was caused by a group of microörganisms known as the Gaertner bacteria, of which the paratyphoid bacterium is a type.

In recent years Rosenau and his associates, after an exhaustive study of the subject, have concluded that the term "ptomaine" is entirely a misnomer, and have been unable to find any evidence of the existence of decomposition products produced in food by bacteria which are poisonous when taken by mouth. It is now recognized, therefore, that the so-called ptomaine poisoning is caused entirely by infection and can be prevented by the ordinary precautions demanded for the prevention of infection. Bacteria of this class are not spore formers and hence do not survive the heat of processing canned foods.

During the last few years the *B. botulinus*, long known in Continental Europe, has been found in this country and has caused a number of cases of illness and death. This is the only spore-bearing organism which produces substances that are poisonous when taken by mouth. Although the growth of this organism is not limited to canned foods, and although it has been encountered more commonly in home canned products than those packed commercially, it has remained for the canning industry to finance the investigation of the subject that has been made in this country. This work has been conducted by the Harvard Medical School in the eastern states and by the medical departments of the University of California and Stanford University on the Pacific Coast with the coöperation of the U. S. Public Health Service. A comprehensive monograph will soon be published describing the outbreaks of botulism in this country, and treating of the occurrence of *B. botulinus* in nature.

Nutritive Value of Foods

Until recently the nutritive value of foods was thought to be measured by their content of protein, carbohydrates, fat, and mineral constituents. In this respect canned foods cannot be differentiated from the same foods stored in the raw state. Since the important role of vitamins in foods is now unquestionable, their consideration with reference to canned foods raises many questions which have not been answered.

The early workers on this subject stated that certain foods lost their vitamins when heated to a temperature of 120° C. and that canned foods were deficient in vitamins. The more recent work does not confirm this. It is now believed that the amount of vitamins A and B is only slightly reduced by the heat of processing canned foods; and that the antiscorbutic vitamin is more sensitive to heat but may be as sensitive to oxidation as to heat. Therefore it seems probable that ordinary cooking in an open kettle may be as destructive of the latter as the processing of canned foods. This can only be conclusively determined by dividing a single lot of a raw product into two portions, cooking one in an open kettle and exposing the other to the canning process and then determining the vitamin content of each.

We know little about the influence or variety of conditions of storage upon the vitamin content of our raw fruits and vegetables. It has been shown that milk varies enormously in its vitamin content because of the varying food given the cow. Some vegetables lose their vitamins gradually when stored in the raw state. Hence it is important that a broad study be made of the vitamin content of all of our foods, not only when freshly harvested but also under all conditions of production and storage, both of the raw product and of the manufactured food.

As a single illustration, if we wish to consider the vitamin content of tomatoes, we are confronted by the effect of variety, locality, soil fertility, degree of ripeness and, closely related to it, ripening off the vine as is customary with tomatoes shipped north in the winter season, home cooking, canning, drying and subsequent storage. With other vegetables these and additional questions must be considered in a like manner.


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We know that after three years of storage canned tomatoes are almost, and possibly entirely, as rich in the least stable of the vitamins as when first canned. Little has been done to determine the amount of deterioration of the vitamin content of raw products during storage, but in a few cases this has been shown to be considerable. This question therefore suggests itself: May vitamins be preserved better by storing the raw product or by canning it before storage? The data now available do not enable us to answer this question.

Processing Studies

The operation known as processing (sterilizing) canned foods was developed by the cut-and-try method. Samples of the foods in cans of various sizes were heated at different temperatures and for different times and the cans held in storage to determine whether spoilage would occur. A temperature and time of sterilization which was found to be sufficient to keep the food, and which yielded a product of acceptable appearance and flavor, were adopted as satisfactory and used in canning the product. If it developed later that more or less spoilage occurred, the temperature or time was increased. Only in recent years has it been fully appreciated that the processing of canned foods is a complicated operation and the study of its fundamental principles undertaken.

BACTERIOLOGICAL STUDIES—The characteristic feature of the canning operation is the destruction of the bacteria by means of heat. Therefore it is of the first importance to know the time and temperature of the process necessary with each food to destroy the most resistant bacteria. When this question was taken up three years ago we found that no methods were available for determining the thermal death point of bacteria at temperatures above the boiling point of water. The first step, therefore, was the development of such a method. The bacteria causing the spoilage of a considerable number of canned foods were then isolated and their thermal death point determined. Those that were found to be the most resistant to heat were subjected to an intensive study at various temperatures, in the juices of typical foods, as well as in phosphate solutions of different hydrogen-ion concentration. The work should be extended to non-spore-bearing bacteria at temperatures below the boiling point of water, as well as to yeasts and molds, in order that we may have information regarding the sterilization of acid products, such as fruits and tomatoes, that is comparable to the information now available regarding foods of lower acidity.

The time and temperature necessary for sterilization are profoundly influenced by the number of bacteria present. It is therefore important to know the conditions which tend to increase the number of bacteria in the raw product. We should know the sources of resistant bacteria, and with this in view studies should be made of the raw product, of all portions of the canning plant, and of the water supply. A beginning has been made on these studies, but much remains to be done.

HEAT PENETRATION STUDIES—A complete knowledge of thermal death points would be of no practical value to the industry without an understanding of heat penetration. The transfer of heat to the center of the can depends on several factors, including the nature and consistency of the food. When a batch of cans is placed in the retort the outer portion of the contents of each can heats rapidly, but the penetration of heat to the center of the cans is sometimes greatly delayed. In processing canned foods it is obviously necessary that all portions of the can be heated sufficiently to effect sterilization. In order to apply the thermal death point of resistant organisms mentioned above to the sterilization of canned foods we must therefore know the temperature of the center of the can during the entire period of processing.

The temperature of boiling water or even 80° C. (176° F.) is sufficient to sterilize if continued long enough. The time required would be so great, however, as to make sterilization at low temperatures impracticable. For instance, a process of eighty minutes at 121° C. (250° F.) is sufficient to sterilize No. 2 cans of corn containing the more resistant thermophilic bacteria. At the temperature of boiling water, twenty-five hours would be required to give a process of the same sterilizing efficiency.

In order to understand the sterilizing value of a certain time and temperature of process, therefore, we must have the heat curve of the center of the can throughout its period of heating. It is also necessary to understand thoroughly the heat distribution of different types of pressure kettles employed.

This work was made more difficult by the fact that canned foods are sterilized after the cans are sealed, and it is still further complicated by the continuous cookers now employed with many products in which the cans rotate while passing through the sterilizer. In undertaking the work it was necessary to develop pyrometers which could be used in determining the temperature of a sealed can when enclosed in a sealed retort, and if necessary while the can was rotating and being heated at any desired temperature and while it was located in any desired portion of the sterilizer.

In this way heat penetration curves have been established for many kinds of canned foods packed in different ways and processed under different conditions. These curves are of little value by themselves. Considered, however, in connection with the thermal death points of resistant bacteria and with the acidity of canned foods during the period of processing they are of value in the fundamental study of the subject.

Material progress has been made in the study of heat penetration, but much remains to be done.

ACIDITY OF CANNED FOODS—A third factor in processing is the acidity of foods. The heat-resistant, spore-forming bacteria will not grow in foods as acid as tomatoes or the ordinary fruits. Moreover, all bacteria are killed in acid fruits and tomatoes by heating for a short time in boiling water. On the other hand, foods of low acidity, like the ordinary vegetables, can be safely processed only at higher temperatures in pressure cookers.

The acidity (hydrogen-ion concentration) of the juices of the majority of canned foods has been determined. The data thus obtained are of value in establishing the process necessary for sterilization. The acidity of the juices of canned foods, however, varies somewhat from that of the liquor of the food during sterilization. With foods that are well buffered, the acidity increases during processing because of the influence of heat. With foods that are not well buffered, such as fruits and some root vegetables, the acidity of the liquor of the can is not appreciably changed by heat, but increases owing to the diffusion of the juices into the liquor surrounding the solid pieces of fruit. In nearly all canned foods, therefore, the acidity of the free liquor increases during processing, and we should have full information regarding the acidity of the liquors of canned foods during the processing period.

This question has been studied in the laboratory with reference to a number of typical foods. The work should be greatly extended and as far as possible carried into the field and studied under commercial canning conditions.

STERILIZATION OF CANNED FOODS—By combining the curves representing thermal death point and heat penetration, taking into consideration the time required for heating the retort to the temperature desired for sterilization, it is possible to calculate the time and temperature which should be necessary theoretically to sterilize a certain food when contaminated by a certain bacterium, the sterilization being accomplished under prescribed conditions.

Such calculations are now being made and make possible a critical study of the processes now used in the industry. They show the importance from the standpoint of sterilization of technological details which are not usually considered to have sterilizing value. For instance, the initial temperature of the center of the can; the length or character of the exhaust; the heating of the retort (when not already hot) before filling it with the food to be sterilized; the accuracy of the retort thermometer; all influence the time and temperature of process necessary to effect sterilization, and an approximately quantitative statement regarding the influence of each may now be made.

The value of such theoretical processes, however, lies chiefly in the fact that they make practicable an intensive study of sterilization that would otherwise be almost impossible because of the amount of work involved. Such a study can best be made by inoculating cans of various foods with a definite number of bacterial spores of known resistance to heat and determining the time and temperature of heating under commercial canning conditions necessary for their destruction. The theoretical process time mentioned above serves as a guide in processing inoculated cans, and greatly reduces the amount of experimental work necessary to determine the proper process.

Several such experimental packs with inoculated cans have been put up, and the results confirm the value of the calculated process times mentioned above and show the practicability of combining the two methods of procedure.

This work should be greatly extended. Experimental packs with inoculated cans should be put up with foods of different kinds in different sections of the country. In one pea-growing region a process of thirty-five to forty minutes at 116° C. (240° F.) is believed to be required to sterilize peas, while in another from twenty to twenty-two minutes are believed to be sufficient. In some corn districts it is recognized by canners that a process of from seventy-five to eighty minutes at 121° C. (250° F.) is required to sterilize corn, while in other localities it is held that a shorter process is sufficient. In each case the hydrogen-ion concentration of the product of the two localities is substantially the same and there is no apparent reason from the nature of the product why they should not require the same process.

In one case where this question has been studied by means of inoculated cans, it was found that the shorter process for peas mentioned above did not kill the resistant bacteria which had been found to cause spoilage in other localities. The process employed in that district, therefore, was not sufficient to insure sterilization. The bacterium with which our experimental cans were inoculated is widely distributed, and may be expected at any time on the peas of the locality in which this work was done. When it appears, spoilage is likely to occur.

The bacteria referred to in this connection are nonpathogenic and are far more resistant to heat than any pathogenic bacteria. There is therefore no question of public health involved, but the amount of spoilage caused by bacteria of this type is sometimes considerable, and is recognized as a matter of importance in the industry.

Preheating and Exhaust

With almost all products the cans are sealed hot in order that after processing and cooling a partial vacuum will remain. Some products are preheated and filled into the can hot. Others are filled cold and a hot brine or sirup added. Still others are "exhausted," that is, they are passed through a steam box or hot water bath after filling and before sealing.

During recent years it has been learned that some form of preheating is important with many products for other reasons than securing a partial vacuum. With some products of slow heat penetration the temperature of the center of the can does not reach retort temperature during the entire period of processing. In such cases the sterilizing value of the process is greatly increased by having a high initial temperature.

Some fruits have a considerable amount of air in their intercellular spaces, and if canned in that condition the oxygen accelerates corrosion and increases the perforation of the cans. The presence of an undue amount of oxygen within the can causes discoloration with some products and with others produces an undesirable flavor.

The information thus far available on this subject is of a general nature and rather superficial. Much yet remains to be done. A study should be made of the gas content of various fruits and vegetables while in the fresh state and under different methods of storing. A study should also be made of the influence on the gas content of exhausting by different methods and under different conditions. The relative merits of steam and hot water exhaust are only partially understood. The relative merits of exhausting at different temperatures and for different lengths of time should receive more attention.

Discoloration of Canned Foods

It sometimes happens that canned foods or the cans containing them develop some type of discoloration, either during processing or during subsequent storage.

When foods of high protein content are heated a trace of hydrogen sulfide is liberated, which gives rise to several forms of discoloration in canned foods. With some varieties of beans hydrogen sulfide combines with the tin and forms a more or less dark discoloration over the entire inner surface of the can, except that bordering on the air space at the top of the can.

With other products the hydrogen sulfide liberated from the protein by the heat of processing passes into the air space and combines with the iron in the top of the can, forming black pulverulent patches which may either adhere to the plate or be rubbed off into the contents of the can. Such discolored patches are found most commonly in canned corn, but are also found in lobster, shrimp, and some varieties of fish. The cans used with shell-fish are sometimes lined with a parchment paper and in that way the discoloration mentioned is partially controlled.

With corn it has been found that the presence of air greatly increases the amount of discoloration formed and that every possible precaution should be taken to insure the tight sealing of the can. The presence of eight or ten milligrams of zinc coated on the top of the can has been found to reduce greatly the amount of iron sulfide discoloration produced in experimental packs.

The amount of this discoloration experienced by corn canners is still a source of annoyance, and any progress that may be made in overcoming it will be of value to the industry.

It has recently been determined that the black discoloration in canned sweet potatoes is due to the oxidation of the iron of the can and its subsequent reaction with some substance resembling polyphenols which occurs localized in the potatoes. This discoloration may therefore be entirely eliminated by properly filling, exhausting, and sealing the cans.

Black hominy has long been a source of great annoyance to packers of that product. It is due in part to the low hydrogen-ion concentration produced by lying the corn to remove the hull. A method has recently been suggested for controlling this difficulty at least in part, by shortening the lying period and completing the dehulling by mechanical means. This method has been developed on a laboratory scale but has not been tried on a commercial scale, and should receive further study.

A pink discoloration is sometimes found with certain canned fruits, as for instance with peaches and pears. This is sometimes the result of excessive sterilization but may be connected with the variety of fruit, the degree of ripeness, and possibly with the location in which the fruit is grown. Discoloration of this type is infrequent and is imperfectly understood.

INFLUENCE OF HARD WATER

It is known that hard water, when used for blanching peas or beans or for the preparation of brine added to the cans, increases the toughness of the canned product. This influence is apparent immediately after canning but becomes more pronounced with storage.

Thus far only preliminary work on this subject has been done. We know little about the influence of waters of medium hardness on the toughness of canned legumes, and except in the case of waters that are distinctly hard we cannot determine by the analysis of water whether or not it will be advantageous to instal a softening process.

TIN PLATE

During the last ten years a systematic study has been made to determine the character of the tin plate best adapted to packers' cans. This question is exceedingly complex and difficult.

No methods have been developed by which plate may be examined in the laboratory and its suitability for the manufacture of cans determined. The only method of testing the service value of the plate is to manufacture it into cans and to pack food in the cans and study both containers and contents at intervals during protracted storage.

The influence of variations in the method of constructing the can, as well as of storage conditions, and the varying action of different kinds of foods add to the complications and make the study almost infinitely complex.

MANUFACTURE OF STEEL BASE—The steel used for the manufacture of tin plate should be as free as possible from segregation and sufficiently soft so that the plate can be sent or rolled without cracking. It is believed by steel manufacturers that tin plate should be made from steel having the following average composition:

Carbon less than 0.2 per cent
Sulfur less than 0.05 per cent
Silicon less than 0.025 per cent
Phosphorus from 0.05 to 0.1 per cent

It is not known whether a materially better quality of plate would result from the manufacture of steel containing any of these constituents in smaller amount. Further work is needed in studying the influence of variations of the constituents mentioned above on the service value of the can.

We do not know whether a heat of steel which is brought to the desired composition quickly and with a minimum amount of "working" gives better results when manufactured into tin plate than a heat which has been badly made and which is brought to the proper composition only after repeated furnace additions.

Both Bessemer and open-hearth steel are used for making plate. The Bessemer steel is ordinarily used only for making the can bodies, while the open-hearth steel is usually employed for the ends, which are subjected to bending strains and require a higher degree of flexibility than is necessary for the bodies.

Better results seem to come from steel annealed at temperatures of from 1200° to 1400° F. than when the annealing is done at higher temperatures, but information on this subject is fragmentary.

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The steel is usually first rolled out in the blooming mill, where it is worked all directions until a bloom five or six inches square is made. The bloom is then rolled down into sheet bar. In some mills, however, the ingot is rolled directly into sheet bar, and in this procedure is not turned and rolled on all sides as in the blooming mill. The influence on the service value of the can of these variations in methods of rolling has not been studied.

It is well known that with heavy cold rolling a sheet can be produced of so hard and smooth a finish that the same weight of tin appears to give it a heavier coating after tinning than one cold rolled to a less extent. Whether the coating adheres to the plate as well, and whether the resulting plate gives as good service in cans as when softer cold rolling is practiced has not been determined.

COATING OF BLACK PLATE—During the last generation there has been a great change in the methods employed in making tin plate. We are not familiar with the methods employed in Wales forty or fifty years ago, but we know in a general way that after the black sheet was pickled and washed it was heated in an oil bath for some minutes before being introduced into the tin pot. After being dipped into molten tin it was heated again in an oil so that the excess tin might drip from the plate.

According to the present practice the plate after pickling is held in a bosh of water slightly acidified with acid until it is taken to the tin pot. The tin pot contains a partition reaching from the top of the pot to a point below the surface of the molten tin. On one side of the partition the tin is covered with zinc chloride and on the other side with palm oil. The black plate passes into the molten tin through the layer of fused zinc chloride, goes under the partition mentioned above and passes out through the layer of palm oil. In this way it reaches the molten tin without previous heating, is only in momentary contact with the tin, and leaves the pot while still hot.

The black plate is more or less porous, and during the pickling operation these pores probably become filled with hydrogen gas. Under some conditions, which are only partially understood, it is believed that this gas may interfere with the perfect coating of the plate, in some cases causing blisters.

A study of modifications of the methods of tinning and their influence on the service value of the cans should be made. It is conceivable that if the plate were heated before being introduced into the tin pot, as was the practice in the oil baths formerly used in Wales, the gas might be eliminated from the pores of the black plate to such an extent as to increase the service value of the latter when made into cans. Moreover, it is possible that such heating might so improve the surface of the black plate that a more continuous coating would be secured.

The amount of tin on the grade of plate used in the majority of packers' cans is probably not sufficient to permit the tin to flow and increase the continuity of the coating if heated in an oil bath after tinning. Still some experimental work on this subject should be undertaken, studying the influence of heating for a number of minutes after coating on the service value of cans made from the plate.

After the plate leaves the tin pot the palm oil adhering to it is removed by means of bran or some other absorbent material. Sometimes peanut shells are used, and since they always contain some sand the plate cleaned with them is scratched. These scratches greatly increase the susceptibility of the plate to rust, and are readily apparent whenever a sheet of plate begins to rust.

It has been determined that the weight of coating has a profound influence on the action of fruit acids in perforating tin cans. Heavily coated tin plate resists perforations longer than plate of ligher coating. This fact suggests the advisability of a study to determine whether plate cleaned with peanut shells, and hence covered with scratches, is more susceptible to perforations than plate cleaned with bran.

ENAMELED CANS—Red fruits are more or less bleached when packed in ordinary cans. For this reason it has become customary to enamel the inside of cans intended for packing red fruits. Such enameled cans protect the color of the fruits, but are much more susceptible to perforation than plain cans. The reason for this is not understood. Walker has suggested that it may be due to depolarization by the unsaturated carbon bonds of the oil used in the manufacture of the so-called enamel. This question should be studied further. A coating is described which will protect the color of the red fruits and will lessen rather than increase the susceptibility of the plate to perforation.

PERFORATIONS—When canned fruits are stored, the fruit acids attack the tin plate to a greater or less extent. Sometimes the corrosion is general, attacking the entire surface of the can to an apparently equal extent. At other times the corrosion seems to be localized and results in holes being eaten through the plate in a relatively short time.

As has been already stated, some products which do not perforate plain cans give serious trouble when packed in enameled cans. During recent years we have made progress in the study of perforations, but much yet remains to be done. The amount of oxygen in the can has a profound influence on the formation of perforations. When cans are loosely sealed, so as to permit the entrance of air, perforation occurs quickly. With some products a beneficial effect is produced by removing a portion of the air by means of preheating.

There are other factors involved, however, than the character of the tin plate, the amount of air present, or the kind and amount of acid in the fruit. What these factors are remains to be determined.

The Pioneer's Field in Petroleum Research

By Van H. Manning

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In order that the picture which I wish to present to you may be adequately visualized we must concede that from the time of the first commercial "discovery" of oil in the United States the resultant industry has been one of continuous expansion and the pioneers of this industry have set a beacon of order and efficiency which lights the highway to progress; a superphase with invaluable applications to the problems of humanity in this great industrial age. These pioneers have been engaged in a contest of discovery and invention which has meant systematized methods in production and in the development of processes of utilization. Looking backward, we can say of these American pioneers that their spirit of adventure into the unknown caverns of the earth and through the uncharted seas of science has within the short space of a few years brought about incalculable and beneficial advancement to the peoples of the world. With this record before us we now turn to the realm of the future, a future accentuated by a universal demand for greater efficiency and economy in the production and utilization of a wasting asset. I am not so bold as to prophesy the future, but I do assert that we have not reached the goal of scientific effort in developing to their fullest degree the petroleum resources below and above the ground—and as the subject of my address implies a field in petroleum research, I revert to the reports which I have made to the Board of Directors of the American Petroleum Institute since August 1919, on the subject of "Improvements in Methods." In these reports there was outlined in a general way a plan for the conduct of the work which should be fostered by the Institute. This work comprehended the technical field of petroleum and natural gas. As a general rule, governmental and state agencies, research foundations, industrial laboratories, and educational institutions have been making their investigations and researches independently. I make no attempt to analyze the character of the work of these organizations except to say that they have accomplished work of the very highest quality and the present technic in the petroleum industry is the outgrowth of these many agencies; however, many of the results obtained have been at the expense of much unnecessary duplication of effort and financial loss. It is realized that there is some research work subjected to limitation of secrecy or a dominant exclusive control of processes, but whatever may be the policy as to the trade secrets, exclusive control by the industry, or secrecy in institutional research, it is my opinion that there is an urgent and immediate need of a promoting and coördinating agency to foster general petroleum research and which will accelerate the acquisition of information to be obtained from the various research organizations of work in progress and contemplated. Quantity of research may be increased and the quality thereof enhanced through proper coördination and supervision.

A hearty coöperation may be expected from the scientist if he can be assured that the results of his investigation are given publicity.

As director of research of the American Petroleum Institute, I have received many recommendations as to the character of research that should be undertaken and without authorship or justification and without attempt to classify these problems as to the order of importance or according to their merits, I submit them to the corporations, the individuals, the chemists, and the engineers for their consideration. It is to the open field of prospecting that I am trying to direct the scientific discoverer. It may be that some of these problems are old and some are new, but in whatever category they fall, a discussion which I hope will follow these recommendations will be disclosed by those who have been the pioneers of the past.

As one who can speak with authority on some of the lessons we learned from the war, I want to say to you directly that the greatest lesson of all to me was the mobilization of the scientific experts for chemical warfare investigations which was so quietly, quickly, and efficiently accomplished and which developed into a technical enterprise of tremendous importance and of which so little has been said. Such an accomplishment has its influence on a peace-time program which I now offer to you.

The following are suggestions from American research chemists and engineers.

The petroleum problems in this list are subdivided under the four operating branches of the industry:

1—Production.
2—Transportation and storage.
3—Refining.
4—Marketing and utilization.

Each problem is classified as an "A" or "B" problem. "A" problems are of known importance, the solution of which will be of material benefit to the industry and the nation; "B" problems are of indeterminate importance and arise through a lack of knowledge; study and solution of these problems may or may not develop results of practical value.

PRODUCTION PROBLEMS

1—An investigation of the use of charcoal, silica gel, and iron gel for the recovery of gasoline from casinghead and refining gases, including an examination of the character of the recovered product and the thermal efficiency of the process in comparison with oil recovery methods. (B)

2—A broad study based on thermodynamic principles of gasoline recovery processes including the application of refrigeration to casinghead and refining gases and development of more efficient methods and mechanical equipment in a manner similar to the work of Norton in recovering helium from natural gas. (A)

3—An investigation of blending volatile casinghead gasoline and naphtha with special reference to the economic limits of blending. (A)

4—Breaking up of water-oil emulsions with maximum oil recovery and the prevention of ingress of water into the oil well. (A)

5—Increasing recovery from wells; reviving old wells. (A)

6—A chemical study of underground water in relation to oil production. (B)

7—Shale oil development. (A)

TRANSPORTATION AND STORAGE PROBLEMS

1—A comprehensive study of fire fighting and prevention methods with respect to all phases of the petroleum industry. (A)

2—Study of methods for cleaning and freeing tanks and bunkers of inflammable vapors prior to making repairs; the development of simple methods for testing such tanks to determine if they have been freed from vapors. (A)

3—Study of the protection of men from noxious gases and other hazards in the entire petroleum industry; use of gas masks, breathing apparatus; designing tanks and apparatus so that men need not enter the noxious atmospheres. (A)

4—Investigation of storage and transportation losses and development of methods for minimizing this loss. (A)

5—Effective vapor pressures in tank cars, etc. (A)

6—Thermal expansion of petroleum as affecting measurements. (A)

7—Cement storage tanks. (B)

REFINING PROBLEMS

1—Recovery of gasoline from refinery gases. The importance of this problem has already been recognized and recovery plants (generally of the absorption type) are in use in various refineries for the removal of gasoline from still gases. An educational campaign should be instituted to advise refiners of the advantages of this procedure and, in addition, the recovery of gasoline from all refinery gases, pressure stills, agitator tanks, etc., should be considered. Relative efficiency of solvent absorbents, charcoal and silica gel and ferric hydroxide gel should be investigated. (A)

2—Recovery of other chemical products from refinery gases:

(a) Propylene and ethylene for making alcohols, glycols, etc. (B)

(b) Chlorinated products, artificial resins, isoprene. (B)

3—Recovery of chemical products from acid sludges. (B)

4—Conservation of chemicals used in the treatment of petroleum products:

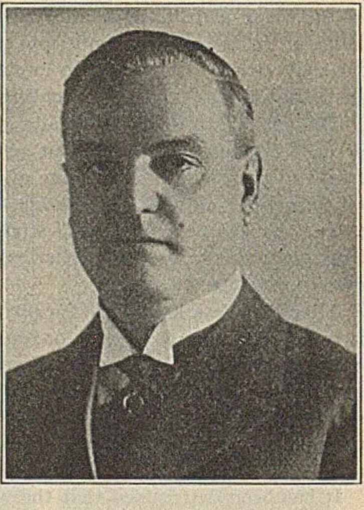
(a) Decreased use of sulfuric acid. Many products are probably treated more heavily than is necessary to insure satisfactory utilization. (A)

(b) Closer utilization of alkali. Many refiners simply make sure they have an excess in their treaters and do not attempt to hold this excess down to a satisfactory minimum. (B)

(c) Wider use of sulfuric acid recovery plants. Application to needs of small refineries. Investigation of best type of equipment. (A)

(d) More economical use of filtering clay and fuller's earth. (A)

(e) Study of most favorable conditions, temperature, time, etc., for chemical treatment. (B)



VAN H. MANNING

5—Increased fuel economy (fire box to oil). There is a notorious waste of fuels in refineries. Extended investigations of proper fuels and of furnace design will result in saving much fuel. (A)

6—Improved design and insulation of stills and fractionation towers. Heat losses can thus be cut down and efficiency will be increased. (A)

7—Utilization of heat liberated in condensing the vaporized oil. Considerable heat is now lost which can be saved by suitable preheaters or heat exchangers. (A)

8—Increased use of continuous distillation equipment. Development work with different types of oils is required to extend use of continuous distillation. (B)

9—Increased use of continuous treating equipment which when fully developed for various oils will result in greater efficiency of operation. (B)

10—Increased use of fractionating columns on stills will give larger yields of valuable gasoline fractions. There is need for thorough scientific investigation of fractionating columns. (A)

11—The prevention of entrainment by more efficient separating devices. The adoption of such equipment will permit much higher distillation rates than those now customarily employed. (A)

12—Development and improvement of cracking processes and increased use of same:

(a) For increased production of gasoline. (A)

(b) For distillation to coke of oils having high content of asphalt. (A)

(c) For production of lubricating oils as through use of $AlCl_3$ or similar agents. (B)

13—Improved methods of filtering lubricating oils. Use of other material than Florida clay or fuller's earth and the revivification and more economical use of filter materials. Possibilities of activated charcoal, silica gel, and iron gel should be investigated. (A)

14—The use of solvents for the removal of color from spent fuller's earth. (B)

15—The fractionation of petroleum residues containing paraffin wax into distillate and undecomposed amorphous wax; and the elimination of gummy or asphaltic portions from wax distillate by a distillation or mechanical procedure. (B)

16—Study of nature and distribution of sulfur derivatives in petroleum. Improved methods of removing sulfur from crude oils and distillates especially by the use of absorbing agents and a study of methods for controlling the distribution of sulfur among the various products. (B)

17—A thorough study of the mechanical and chemical efficiency of distillation methods as applied to various types of petroleum with special reference to the development of flexible refining methods which permit the maximum production of products for which there is the largest demand. Under this head is included a study of cracking, topping, and straight cut distillation. (A)

18—A thorough investigation of the progressive deterioration of stills with reference to the prevention of explosions and the reduction of life and fire hazards. (A)

19—Standardization of analytical methods, including improvement of many present methods and development of new methods. (A)

20—Study of physical and chemical constitution of different types of crude petroleum to provide necessary fundamental data now lacking. (B)

21—Study of various chemical reactions of petroleum hydrocarbons, particularly oxidation, hydrogenation, and halogenation. Such study may lead to the manufacture of valuable base materials and intermediates for the production of organic chemicals and dyestuffs. (B)

22—Study of nature and behavior of crystalline and amorphous paraffin wax in petroleum; and investigation of wax chillers. (B)

23—Investigation of production of special products, such as:

(*a*) Harder grades of wax. (B)
(*b*) Wool oils. (B)
(*c*) Polymerized olefins. (B)
(*d*) Benzene and toluene. (B)
(*e*) Organic acids and alcohols. (B)
(*f*) Drying or siccative oils. (B)
(*g*) Isoprene. (B)
(*h*) Dyestuffs. (B)

24—A study of the properties required of oils for use in absorbing benzene, toluene, etc., from artificial gas or in solvent recovery system. (A)

25—Thorough study of the relation between chemical constitution of oil and its lubrication properties with a view to so treating oils as to increase their lubricating power. (B)

26—A physicochemical study of the structure and properties of greases. (B)

27—Study of methods for reducing the viscosity of Mexican fuel oil so as to eliminate the necessity of preheating. (A)

28—Dehydration of crude oils and oil emulsions, including study of comparative efficiency and costs of the following methods:

(*a*) Electrostatic. (A)
(*b*) Centrifuging. (A)
(*c*) Heating. (A)
(*d*) Miscellaneous methods. (A)

29—A study of the influence of various types of electrical discharges and other electrical effects on cracking of oils. (B)

MARKETING AND UTILIZATION PROBLEMS

1—Preparation of rational specifications for petroleum products; these specifications to be based upon the results of actual research work. More rational volatility specifications for gasoline and tests for the "oiliness" property of lubricants are especially desirable. (A)

2—Standardization of analytical methods and apparatus for testing and analysis of petroleum products. (A)

3—Utilization of wider range of motor fuels in mobile types of engines (autos, trucks, tractors, etc.). (A)

4—More efficient utilization of heavy oils in Diesel and other engines of the heavy oil type. (A)

5—Investigation as to the actual need of highly refining gasoline for motor fuel; is it necessary to remove bad smelling sulfur compounds completely in order to obtain efficient service from gasoline? Will these compounds injure the engine? If high degree of refinement proves unnecessary educate the public to use less highly refined products and thus increase the yield and lower the cost. (A)

6—Development of higher efficiency in internal combustion motors through use of selected fuels (naphthene or aromatic mixtures) or through use of chemically treated fuels which will stand higher compressions. Applies especially to aeroplane engines. (B)

7—Modify the design of carburetors and internal combustion engines so as to enable the use of less volatile gasoline, and investigate the relations between volatility, specific gravity, and distillation analysis to performance in automobile engines; relative performance of blended mixtures and straight cuts. (A)

8—A study of the fundamental causes of carbon formation in cylinders; elimination of polymerized products in cylinders; study effect of additions of peroxides, naphthalene, picric acid, phenanthrene, pyrene, picene, cyclohexanol, phenol, etc. (A)

9—Combustion characteristics of different hydrocarbon series. (B)

10—Ignition temperature, detonation, etc. (B)

11—Effect of volatility on fuel consumption. (B)

12—An unbiased scientific study of the differences in properties and behavior of oils from different base crudes and the fundamental causes thereof. (B)

13—A study of the relative tendency of different lubricants to absorb fuel and become excessively diluted. (A)

14—Scientific study of numerous problems in lubrication. (A)

15—Recovery and purification of used lubricating oils in large industrial plants. This would be in the interest of conservation. (B)

16—The prevention of oxidation of mineral oils in transformers. (B)

17—Development of satisfactory small-scale oil-gas apparatus for use in country homes and small villages. (A)

18—Development of household oil heating devices. Why not use oil in the furnace? It should be as convenient as gas with proper equipment. (A)

19—More effective utilization of the butanes and pentanes in natural gas gasoline and in light petroleum fractions. Much of this is now lost by evaporation. (B)

20—Utilization of larger proportion of petroleum coke produced. Owing to impurities much of this coke is not suitable for carbon products. Elimination of impurities and improvement of quality should be investigated. (A)

21—Production of oil-gas and also hydrogen by cracking natural gas, or petroleum vapors with the production of a carbon black that will meet the same requirements as carbon black made by the incomplete combustion of natural gas. (B)

22—A broad physicochemical study of the production of carbon black, with a view to the discovery of more efficient methods than wasteful partial combustion process. (B)

COLLOID CHEMISTRY

In view of the importance of colloid chemistry in connection with the petroleum industry, I wish to stress particularly the need for the study of various problems in this industry from the colloid chemistry standpoint.

As topics for major problems, the following have been suggested, some of which have been mentioned heretofore in this paper; however, it is believed worth while to group them under this heading:

1—A thorough study of the properties and behavior of emulsions including:

(*a*) Mechanism of the formation and stability of various emulsions. (*b*) A study of the nature of emulsifying agents. (*c*) Methods of breaking. (*d*) Comparison of properties of emulsions obtained from different base oils. (*e*) Study of various emulsion products, such as cutting oils and greases.

2—A thorough study of lubrication from a colloid chemical standpoint.

3—Investigation of the properties and behavior of crystalline and amorphous wax.

4—A study of the application of the adsorptive action of various substances, such as bauxite, fuller's earth, silica gel, iron gel, etc., with reference to the following problems:

(*a*) Recovery of gasoline from refinery gases.
(*b*) Desulfurization of both light and heavy fractions.
(*c*) Removal of coloring matter.

5—A thorough study of the properties and utilization of various grades of asphalt.

AMERICAN CHEMICAL SOCIETY SUGGESTIONS

At the meeting of the Petroleum Section of the American Chemical Society which was held in New York City in 1921, the following subjects were recommended as suitable fields for research:

1—The chemistry of petroleum hydrocarbons, particularly of the higher homologs.

2—The chemistry of the sulfur, nitrogen, and oxygen compounds in petroleum.

3—The chemistry of sulfuric acid refining of oils.

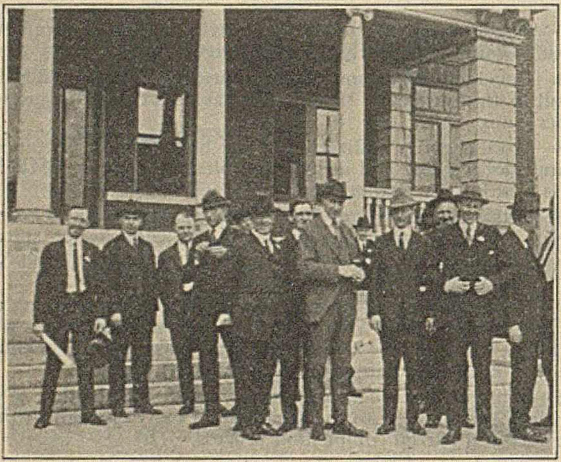
4—The chemical and physical changes undergone by lubricating oils used in continuous systems.

5—The causes and mechanism of color changes in oils.

The list might be supplemented almost indefinitely from the fields of fuel and lubrication.

SUGGESTIONS FROM AN ENGLISH CHEMIST

In considering the directions in which organized scientific research for the benefit of the petroleum industry can now be set on foot, it appears to me that before proceeding to enumerate a series of definite problems for investigation there are some general considerations which ought to be put on record.



GROUP AT SHEFFIELD, ALA., BEFORE VISITING NITRATE PLANTS

At about the middle of the last century the development of the steam engine had reached such a stage that before any further vital improvements could be made and measurements of engine efficiency carried out it became essential that the fundamental physical data relating to the properties of water and steam should be determined with a great deal more accuracy than that attained at the time. The classical work on the steam engine done by Regnault and his colleagues under the auspices of Emperor Napoleon III over a period of about thirty years has been until quite lately the basis on which all computations relating to steam engineering were founded. In my view the time has now arrived when, in the interests of the use of oil fuel of all kinds, particularly in the various forms of internal combustion engine and in large steam boilers, a similar comprehensive series of determinations of fundamental physical and chemical constants should be carried out by a competent organization. With the support of the combined oil interests, an attempt should be made to improve the technic of the various processes of the mineral oil industry, and to this end a comprehensive and systematic series of chemical and physical investigations is required.

1—It is of course known that nearly all petroleum products, whether light, medium or heavy oils or solids, are not simple chemical substances, but complex mixtures, whose single constituents are often difficult to separate from one another. But this difficulty of preparation furnishes no excuse for our present lamentable ignorance of the fundamental properties of many of these important bodies, now consumed to the extent of many millions of gallons annually. I am not exaggerating when I say that the only data we possess as to many of these substances depend on determinations carried out years ago on quite small quantities by investigators whose competence and equipment left much to be desired, and that in many cases the purity of the substances in question was, to say the least of it, extremely doubtful. I think, therefore, the time has now arrived when an attempt should be made to prepare in quantity in a state of high purity all the more important members of at least three of the main chemical series, the normal hydrocarbons having the formulas C_nH_{2n+2} C_nH_{2n} and C_nH_{2n-2}. When these have been properly studied it will then be possible to proceed to a certain number of the iso and cyclo bodies of corresponding formulas. The study should include not only the usual properties mentioned in the textbooks, but determinations of the flash point and firing point of each, as well as fairly complete measurements of the vapor pressure of the more important members from quite low temperatures below the freezing point of the substances up to and beyond their boiling point—in fact, a systematic extension of the classical work of Ramsay and Young.

2—Bearing in mind that practically all commercial oils are mixtures of several homologs, it will be desirable that as soon as the requisite knowledge of the fundamental properties of the pure constituents has been obtained, a study should then be organized on certain mixtures, and that the laws regulating the dependence of the physical properties of a mixture of oils on those of its constituents should be investigated. Thus it is highly desirable that we should know more of the nature of the vapor pressure curves of mixtures, and should be in a position to predict more accurately, for example, the influence on the vapor pressure and flash point of a given addition of low-flash oil to one of lower volatility.

3—Up to the present time the thermal properties of most organic substances have been investigated by means of the calorimetric bomb. In the opinion of many of those who have used this instrument it possesses very grave disadvantages, particularly for application to extremely volatile oils. Indeed, under many circumstances the determination of the heat of combustion of such a substance as petrol by means of this instrument may be dangerous, even though quite small quantities of substance are used. In my view it is urgently necessary that as a preliminary to the program of systematic work outlined above, a design should be worked out for a new calorimeter, which would probably be of the flow pattern in which accurate results could be obtained for the gross and net calorific values of low-boiling organic substances.

4—An urgent requirement of the petroleum industry is that more precise and detailed instructions should be prepared and apparatus devised for carrying out the different standard tests prescribed. In 1912, at the Vienna Congress of the International Petroleum Commission, proposals were made as to the standardization of the different types of flash point tester, and it was shown that the original apparatus as devised by Sir Frederick Abel, the modified form used in the British Colonies, and the later German form differed systematically in their indications by amounts which were too serious to be ignored. The work of the British National Physical Laboratory and of the American Bureau of Mines in investigating the causes of these systematic differences should be continued, with a view, at a later stage, to some ultimate international agreement being arrived at on all the more important tests on the different kinds of oil products.

One of the most urgent directions in which further work of this kind is required is in connection with very low flash points, since the methods and apparatus of Abel are quite unsuited for work at low temperatures. Tests comparable with the Abel test, and a proper form of apparatus for the same, need to be worked out for motor spirit of all grades. In the apparatus for this test a suitable cooling arrangement would take the place of the water bath and burner.

Similarly, the investigation of viscosity by the various types of apparatus in use greatly requires systematizing, and the true relation between viscosity, lubricating value, and chemical composition requires more detailed investigation. In view of the widespread introduction of heavy fuel oil into marine work, the whole question of the viscosity and setting points of heavy oils needs much further systematic study, in order that the problems arising in connection with the storage and transport of heavy oil may be adequately dealt with.

5—It is very desirable that the limits of explosibility of oil vapors with air and oxygen should be more thoroughly investigated than at present, and the influence of pressure and temperature on these limits should be studied over a considerable range.

6—It is well known that in the cracking process the general basis of the reactions occurring is that heavy hydrocarbons can be made to split up into bodies consisting of smaller and lighter molecules. In general it is found that a body of the formula C_nH_{2n+2} splits up into two smaller portions of half the molecular weight. It would, however, in general be more advantageous if the cracking could be so designed that instead of division of a long chain-type molecule into two equal portions, the severance could be made in such a way that the pieces were more like two-thirds and one-third or three-fourths and one-fourth, seeing that nowadays the object of nearly all cracking is to obtain a large proportion of the lightest possible spirit. An extension of such work as that of Rittman in America and of Ashcroft in England, with a view to determining the conditions favorable to the formation of low-boiling hydrocarbons of the paraffin series, as well as of the lower members of the aromatic series, is one of the most urgent lines of new investigation. It should be undertaken, in the first instance, not by engineers but by physical chemists having a thorough knowledge of phase-rule chemistry and reversible reactions. Engineers can afterwards be called upon to build up manufacturing processes upon the foundation thus laid.

The use of catalysts in facilitating the production of lighter hydrocarbons from petroleum should also be systematically studied. Already promising results have been obtained on the application of catalysis to the production of petrol.

7—In the utilization of motor spirit many inconveniences are caused if the spirit in question contains hydrocarbons which tend to become gummy. It is well known that cracked spirit, the use of which is rapidly extending, contains bodies in which spontaneous slow changes may subsequently take place, and a grade of spirit having no objectionable properties when fresh may polymerize or suffer slow oxidation, and the percentage of hydrocarbons of a gummy character may become greatly increased merely on standing. The cause of this phenomenon is very obscure, and it is desirable that the nature of those bodies which are objectionable should be thoroughly investigated and that the changes which go on in cracked spirit, tending to restrict its usefulness, should be properly studied, with a view to mitigate or prevent them completely.

SUGGESTIONS FROM AMERICAN MECHANICAL ENGINEERS. PROGRAM OF INVESTIGATION OF FUELS USED IN INTERNAL COMBUSTION ENGINES

For the purpose of increasing combustion efficiency, reducing noxious quality of exhaust gas, development of wider range of fuel, and reduction of waste through imperfect combustion.

1—Influence of composition of fuels on composition of exhaust gases.

Effect of physical properties of fuel:

(a) Volatility.
(b) Distillation range.
(c) Viscosity.
(d) Density.

Effect of chemical properties:

(e) Chemical composition.
(f) Ratio of carbon to hydrogen.
(g) Degree of unsaturation.
(h) Addition of substances to improve combustion or prevent detonation.
(i) Effect of catalyzers.

2—The behavior in internal combustion engines of liquid fuels produced by different processes.

3—Experimentation with new type engines for tractors and trucks using low-grade fuels, such as topped oils, tars, etc.

4—Adaptation of engine structure to available fuels:

(a) Carburetor.
(b) Manifold.
(c) Compression.
(d) Ignition.
(e) Lubrication.
(f) Stroke, etc.

5—Standardization of oil well supplies.

6—Heat treatment of drill steels and development of improved drilling methods.

An American chemist comments as follows on a few problems selected at random from the preceding list.

DISTILLATION

In the distillation of kerosene, wax distillate and lubricating oils, steam is usually used with direct fire under the still, to prevent decomposition of the hydrocarbon oils treated. A thorough testing of vacuum distillation instead of the use of steam in the refining of kerosene, wax distillate, and lubricating oils should be worked out at a really low vacuum with the view of using low vacuum in the distillation of petroleum oils. The distillation of kerosene, gas oil, and residuum from paraffin, semi-paraffin and asphaltic oils under heat and pressure lend themselves to research so that industrial methods may be worked out to crack oils for general use by refineries.

SPECIFIC HEAT AND HEAT VAPORIZATION OF PETROLEUMS

The specific heat of liquids, latent heat of vaporization, and specific heat of the gaseous hydrocarbons and petroleum oils and their distillation products is of importance to the refiner. With a knowledge of these three physical constants one could calculate the square feet of heating area to a still, furnish construction, condensing areas of vapor lines and water condensing areas in closer agreement with what is required in commercial installations. They would be of high importance in the cracking of petroleum oils, in working up ratios of heating surface of the still to the vapor line, aerial condensers and water condensers per gallon of oil treated, per gallon of pressure distillate, and per gallon of gasoline made per unit of time.

TREATMENT OF DISTILLATION PRODUCTS OF PETROLEUM

Investigation of the use of other acids than sulfuric in the refining of petroleum distillates with a view to finding reaction products which will lend themselves to further chemical products for commercial use. There seems to be no doubt that for certain oils hydrochloric acid would give hydrocarbon chlorides which upon hydrolysis would yield alcohols for use perhaps in the formation of condensation products useful as insulation material and for other purposes.

FILTERING MATERIALS IN REFINING

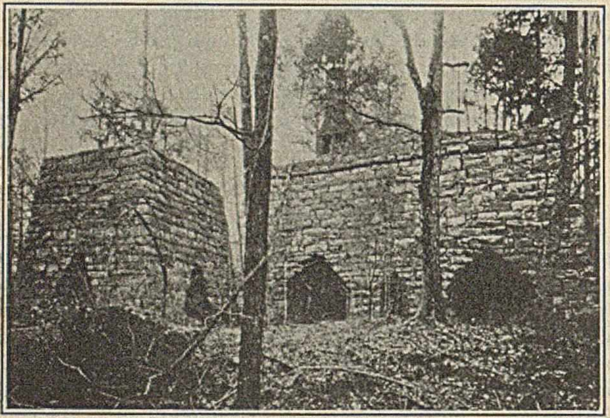
Fuller's earth and a number of re-burnings of the same for re-use with control factors such as microscopic examination during burning. Investigation as to the factors involved such as absorption phenomena as a function of the size of the particles. Also the regeneration of the filtering qualities of the earth while still on the filter bed, instead of sending to "bone burning house" to be regenerated at high temperatures with incident depreciation of its filtering qualities.

SOLVENTS

Sulfur dioxide lends itself to the separation of hydrocarbon groups and should be studied on a semicommercial scale, with a view to separating the particularly interesting groups of naphthene hydrocarbons which are so abundant in some of our crude oils. This might well lead to a whole series of commercial dyes being made, from the naphthenes as a base. Alcohol and other solvents should also be studied.

CONSTITUENTS OF PETROLEUM

The work of Warren and Mabery on the constituents of petroleum oils has been of the highest value to every one connected with the scientific as well as the technical side of the petroleum art. However, our knowledge is meager compared to what is yet undone. For illustration, our knowledge of the constituent hydrocarbons making up lubricating oils is well nigh a blank, and so much depends upon the quality of these oils. A thorough knowledge of the properties of these hydrocarbons would throw a flood of light upon just what hydrocarbons have the lubricating qualities for the specific work in hand—such as for aeroplane use in warfare, where so much depends upon superior oils. To get at the whole lubricating problem, it seems to be necessary to know the hydrocarbons in the lubricating oil before one can state what it is that gives an oil the quality of adhering to two surfaces without breaking down under the temperatures and pressures of the surfaces.



OLD TANNEHILL FURNACE, REPUBLIC IRON & STEEL COMPANY

EMULSION OILS

The production of emulsion oils in the United States is relatively large and much research is necessary so as to break down the emulsion economically. An immense amount of work is ahead to determine the characteristics of the varied emulsion crude oils and bottom settlings in tanks, for millions of gallons are wasted yearly as a result of the difficulty in handling this material. It is not clear as to how the water is dispersed in the hydrocarbon oils, but it seems reasonable to suppose that part of the water is present in the hydrated form, adding to the difficulties of handling the oil due to puking or frothing of the still charge when the hydrate breaks down into water and hydrocarbon liquid at a temperature above the boiling point of water. A suggested research would be to isolate a series of hydrocarbon hydrates from emulsion oils or to make a set from known hydrocarbons of varied molecular weight.

ELIMINATION OF REDISTILLING OF DISTILLATES FROM CRUDE OILS

A large saving in economic wealth could be obtained in the average refinery by installing proper fractionating columns upon the crude still so as to make one cut for finished gasoline without going through the usual redistillation of the crude gasoline ordinarily distilled off the crude. This holds for the kerosene cut also. This method of operation would cut down not alone the fuel cost but also the number of stills for a given output. The uncondensable gas loss in refinery practice is large but would be cut down by making one cut off the crude for its gasoline and kerosene content. The treatment with acid and caustic soda for the gasoline would be eliminated when using Pennsylvania and most of the mid-continent, Kentucky, and Virginia crude.

GAS OIL

More efficient methods of cracking gas oil into marketable gasoline and kerosene so as to cut down the excessive fuel cost involved in producing gasoline by the successful process now in use. Also to work out atmospheric pressure processes by the use of catalyzers. Increase fixed gas yields for heating and lighting purposes, to the gallon of gas oil from gas making apparatus. To utilize gas oil for more economic purposes than fuel oil.

WAX DISTILLATE

The treatment of wax distillate in one stage to convert the amorphous wax into crystalline (so that it will readily press out in the filter presses) in the crude stills instead of the usual practice to recrack the wax distillate in another still cracking the same at atmospheric pressure. Centrifuging experiments for the removal of amorphous and crystalline wax from their hydrocarbon solvent.

FOOTS OIL

Foots oil is an intermediate cut from the wax distillate which is re-cycled and re-cycled in the refinery and contains wax which should be recovered. It would mean tons of wax a day recovery to the industry.

LUBRICATING OIL

The acid treatment of lubricating oils and the treatment of emulsions which occur from neutralizing and water treatment of the same after acid treatment. The distillation of the lubricating oils by means of vacuum instead of use of steam at atmospheric pressure should be tested out for economy and production. The problems in connection with filtering of lubricating oils to color, flash, fire, and viscosity and by the use of filtering materials that have specific action upon the different types of hydrocarbon, instead of as at present the use of fuller's earth and boneblack, would be valuable. Also the investigations of solvents for the refining of lubricating oils instead of acid and caustic treatment in filtering such as liquid sulfur dioxide and other solvents.

CASINGHEAD GAS

To work up a series of commercial solvents which will have selective solubility for specific hydrocarbons in the casinghead gas so as to utilize the same for other purposes than internal combustion engine use.

COLOR OF HYDROCARBON OILS

To determine the color from light lemon to deep red of the various petroleum products and what the colors are due to with a view to making water-white lubricating oils. My present view is that the color in the main is due to colloidal carbon. However, this has not been determined experimentally.

TESTS OF PETROLEUM PRODUCTS

The present control of petroleum products is highly variable on account of the human element, making it difficult to check results in different parts of the country apparently using the same instruments. It seems necessary to work out tests that are practically mechanical in their operation, readily duplicable by any two operators and cutting out highly skilled technicians.

SULFUR OILS

Many suggestions have been made that investigations are necessary of the sulfur oils and gaseous products coming off the stills. These gases have a deleterious effect upon the health of the men; in addition a form of rash appears upon the skin, and they also cause conjunctivitis. It has been found that vapor and gases from the crudes containing a high sulfur content have a narcotic effect upon the workmen. The constituents of these gases are not known. It is known, however, that hydrogen sulfide is present but arsine and stibine have not been isolated, and it is of interest that the American Petroleum Institute and the United States Bureau of Mines have just started an investigation to cover the three fundamental factors involved: (1) to determine the constituents of these vapors and gases, (2) the amount of concentration, and (3) a gas mask to be developed to protect the workmen.

Some Physical Properties of Rubber Compounded with Light Magnesium Carbonate[1,2]

By H. W. Greider[3]

Mellon Institute of Industrial Research, Pittsburgh, Pennsylvania

Light magnesium carbonate is a light inorganic filler for rubber which has heretofore received little attention from American rubber technologists. In this paper there are given data showing that this material behaves as a typical reinforcing pigment, increasing the tensile strength, hardness, stiffness, and resilient energy capacity of rubber in which it is compounded. Comparison has been made between the physical properties of rubber compounded with magnesium carbonate and with other commercial rubber reinforcing fillers, including zinc oxide, gas black, prepared china clay, and colloidal barium sulfate. The results indicate that magnesium carbonate is exceeded in reinforcing power only by gas black.

Special consideration is given to the principal disadvantage of magnesium carbonate in rubber, viz., the property of high permanent set imparted to the vulcanized product, which is attributable to the definite crystalline or nonamorphous character of the particles. The author believes that the application of the principles of colloid chemistry to the conditions of the commercial precipitation process will enable this material to be prepared in an amorphous form which will make it much more valuable as a rubber compounding material, by reducing the objectionable permanent set and enhancing the tensile strength and toughness of rubber compounded with it.

LIGHT magnesium carbonate, the chemically precipitated basic hydrated carbonate of magnesium, is not a new compounding material to the rubber industry of this country although it has never had the extensive and general use as a toughening and reinforcing filler in American rubber compounding practice which it has found in British and Continental rubber manufacturing. The English rubber chemist's knowledge of and experience with magnesium carbonate is, therefore, considerably greater than our own. The reason for this may be explained by the fact that rubber compounding practice has developed along rather different lines in this country from in Europe, particularly with respect to the adoption of gas black as a reinforcing pigment. The future for gas black does not seem particularly encouraging at this time owing to the rapidly decreasing supply of natural gas available for its manufacture and to various actual or threatened legislative restrictions on the use of natural gas for the production of this material. The rubber industry is, therefore, very properly concerned with the discovery of new, light, inorganic, "active" fillers, and is interested in the further development and improvement of those which it already uses. Some American rubber manufacturers use considerable amounts of magnesium carbonate; others use very little or none at all, and it is believed, therefore, that some of the data here presented, on the physical properties and mechanical behavior of rubber compounded with light magnesium carbonate, will be of interest to those rubber technologists who have not previously given this material much attention or study.

The raw material for the manufacture of light carbonate of magnesia is dolomite rock, high magnesian-limestone, of which there are enormous deposits in this country and, in fact, all over the world, so that there is no possibility of a future exhaustion of the raw material supplies for the manufacture of this product. A number of the deposits which are being worked commercially at the present time are in Pennsylvania, convenient to the manufacturing centers and markets of the Eastern and Central States. The companies now manufacturing light magnesium carbonate have producing capacity ample to supply any possible needs of the rubber industry without the installation of additional equipment. It should be remarked that, since magnesium carbonate is manufactured by a chemical precipitation process, its production cost will necessarily be greater than the costs of naturally occurring materials which require only a minimum amount of treatment to prepare them for use in compounding; the principal factors in the cost of magnesium carbonate being coal and labor, both of which items may be subject to some downward revision in the future.

Basic magnesium carbonate may be manufactured from any soluble magnesium salt by treating it in solution with an alkali carbonate, but the product so obtained is likely to be rather variable in composition and not extremely finely divided. The light carbonate offered to the rubber industry as a compounding material is prepared commercially in this country by the rapid heating of a solution of magnesium acid carbonate, and this process gives a very white, soft, bulky, finely divided form of the material, of uniform composition. The formula ordinarily given for the composition of the substance in the dry form is $4MgCO_3.Mg(OH)_2.5H_2O$, but numerous analyses of the commercial material seem to indicate that it corresponds actually more nearly to such a formula as: $11MgCO_3.3Mg(OH)_2.11H_2O$. The composition varies slightly according to the conditions obtaining in the production processes, particularly the concentration of the magnesium acid carbonate solution and the rate of heating of this solution, but under rigid control of the process the composition of the product will be constant. The commercial carbonate of magnesia is usually practically chemically pure, containing only traces of iron and alumina, no silica, and considerably less than 1.0 per cent of lime as calcium carbonate. On samples free from hygroscopic moisture it gives an ignition loss varying from about 54.5 to 56.8 per cent. At ordinary temperatures it is inert to most chemical influences except the action of acids, which dissolve it, forming soluble magnesium salts. No decomposition takes place on heating to temperatures below 265° C. (509° F.), a temperature much above that to which rubber products may be safely subjected, either in the vulcanization process or subsequently. It seems probable that the water in the above chemical formula for the material is not ordinary water of crystallization, but water of constitution.

With regard to its use in rubber, its volume cost per unit of reinforcing effect, or per cubic foot of rubber compounded with it, will be small, owing to its low density, and considerably less than that of heavy pigments, such as zinc oxide or barium sulfate.

Light magnesium carbonate has an absolute density of about 2.18, although some figures rather lower than this have been given. It is, therefore, one of the lightest of the min-

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[1] Received March 25, 1922. Presented before the Division of Rubber Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

[2] The data presented in this paper summarize the more significant portions of the results of an investigation of this material, carried out at the Mellon Institute of Industrial Research, for the Magnesia Association of America.

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

eral inorganic fillers and gives a vulcanized rubber of low specific gravity, although somewhat higher than that given by gas black or lampblack. The individual crystals have a distinct acicular crystal form and are very friable. Examination under the microscope shows an average particle size of somewhat less than a micron, with a few larger crystals, although the particle size varies somewhat in the product of different manufacturers and will depend on the control of the conditions of precipitation and upon the completeness of the pulverization process. The carbonate shows only a very slight solubility in water, about 0.035 g. of the oxide dissolving in a liter, and giving the solution a reaction alkaline to thymolphthalein indicator.

Except with respect to investigations of the effects of various mineral and organic accelerators, there has been, until recently, but scant information regarding compounding ingredients in the literature of rubber technology. Toughening and reinforcing fillers were, of course, always differentiated in the practical work of the rubber technologist from ordinary coarse fillers and inert pigments, but very little data comparing the actual physical behavior of different fillers in rubber were published until W. B. Wiegand[4] studied the effects on the stress-strain relationships of rubber, obtained with several common compounding materials, and brought forward the concept of energy of resilience in rubber. Wiegand divides all rubber fillers into two groups, according to whether the average particle size is extremely small or whether the particles are relatively coarse. The reinforcing effect of rubber pigments he considers to be a function of the surface area exposed to the rubber by unit volume of the material, aside from specific surface and cohesion effects and, therefore, dependent upon the fineness of division of the particles. He succeeded in showing that all the rubber fillers he studied, which modify the stress-strain curve in such a way as to enable the rubber to exhibit high total resilient energy, are those which are very finely divided. These fillers, which are relatively few in number, he designates as "active" fillers or reinforcing pigments, whereas the coarse fillers, which do not greatly modify the stress-strain curve and, therefore, only dilute the rubber and attenuate its tensile strength, ultimate elongation, and resilient energy capacity, in whatever proportion they may be used, he refers to as physically inert fillers. Resilient energy capacity, according to Wiegand, is a measure of the reinforcing or toughening effect obtained with various fillers and he relates it also in a theoretical way to abrasive wear resistance.

Wiegand did not include light magnesium carbonate among the rubber pigments studied by him, and aside from mere occasional mention of its action as a mild accelerator of vulcanization, the work of C. O. North[5] seems to be the only investigation so far published in which the behavior of this material in rubber is described. North made a comparative study of zinc oxide, gas black, magnesium carbonate, lithopone, barytes, and tripoli flour, in mixes containing rubber and sulfur only, with respect to the effects of these fillers on the physical properties of the vulcanized rubber. He found that, in the type of basic mix he used, magnesium carbonate gave its maximum effect on tensile strength at six volumes of the carbonate to each one hundred volumes of rubber, this tensile being higher than that obtained with any other filler, except gas black. For proportions of magnesium carbonate between six and fifteen volumes per one hundred of rubber, he obtained values for tensile strength "corrected" to the basis of 100 per cent rubber in the stock, which were equal to or slightly greater than the highest values obtained for zinc oxide, but not as great as given by larger proportions of gas black. For the same proportions of magnesium carbonate he obtained calculated values for tensile product, and for tensile product "corrected" to 100 per cent rubber, which were greater than similar values obtained for gas black, zinc oxide, or the other fillers studied. This last result means, of course, that magnesium carbonate gives rubber having high tensile strength combined with high ultimate elongation values. North also gave data showing the high permanent set given by magnesium carbonate and attributed to this effect the fact that American compounders had not used this filler to a very great extent.

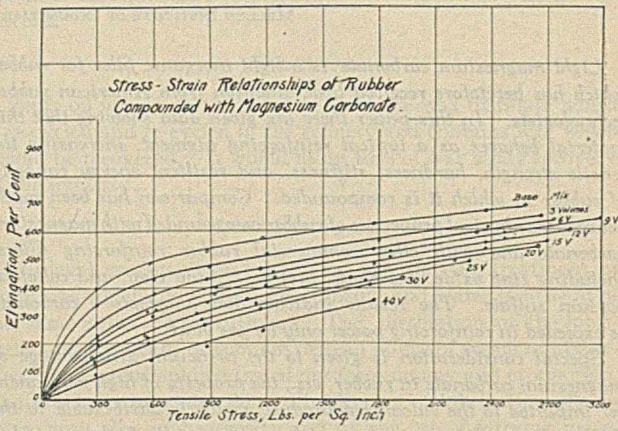

FIG. 1

EXPERIMENTAL METHOD

All the rubber samples described in this paper were prepared under experimental conditions maintained as nearly uniform as possible, with respect to the composition of the basic mix, incorporation of the fillers on the mill, calendering, and vulcanization. The basic mix adopted had the following composition in parts by weight:

First quality pale crepe	100
Litharge	30
Sulfur	5

This basic mix is similar to that used by Wiegand in the investigation referred to above, except that pale crepe rubber was used in place of fine Para. The difficulty in obtaining a satisfactory grade of cleaned and dried Para at the time this work was begun made this change seem advisable. In parts by volume this mix contains:

First quality pale crepe	100
Litharge	3
Sulfur	2.5

The purpose of using this type of basic mix containing a considerable excess of litharge as accelerator was to make it possible to cure all the samples for a fixed period of time and to avoid the preparation of a series of cures for each proportion of filler of which the effect was to be studied. The values obtained for physical properties should also be somewhat nearer to those which can be produced in the factory than is likely to be the case in samples cured for a longer period with sulfur only, where the harmful effects of the longer period of heating on the samples may vitiate the results.

In this work two different lots of pale crepe rubber were used. The first lot, used in preparing samples compounded with various proportions of magnesium carbonate, gave a practically flat state of cure curve (judged from tensile strength values) over a curing period from 40 to 50 min. at 42 lbs. steam pressure (143° C.) when the samples were vulcanized in one-eighth inch thick sheet-molds in a press at 2500 to 3000 lbs. pressure. The basic mix sample showed its

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[4] *Can. Chem. J.*, **4** (1920), 160; THIS JOURNAL, **13** (1921), 118.

[5] *India Rubber World*, **63** (1920), 98.

optimum aging qualities, both with respect to accelerated aging and weathering tests, when cured 45 min., and the same was found to be the case when the stock contained 15 volumes magnesium carbonate, and this was, therefore, selected as the curing period for all samples prepared from this lot of rubber. The second lot of rubber used in preparing stocks in which magnesium carbonate and other fillers were compared, was found to give its optimum cure, both with respect to tensile and aging qualities at a 49-min. period, which was, therefore, adopted as the best cure for all samples prepared from that lot. It was found, in curing samples prepared from both these lots with sulfur only, that both were decidedly slow curing in the absence of an accelerator. No difficulty was experienced in obtaining satisfactory cures in the litharge-pale crepe mix described above and the results obtained may easily be duplicated. The excess of litharge used was sufficiently great so that no difference in the cures when larger proportions of magnesium carbonate were used was observed, although North's[5] data showed that in a rubber-sulfur mix the accelerating effect of the larger proportions of magnesium carbonate was quite appreciable. Rubber cured with an excess of litharge accelerator was found to be considerably stiffer and much less extensible than when cured with sulfur only.

Three series of rubber samples were prepared to obtain the data given in this paper. In the first series the samples were compounded with proportions of magnesium carbonate varying from three to forty volumes per one hundred volumes of rubber in the compound. In the second series light magnesium carbonate in the proportion by volume found to give the maximum reinforcing effect (nine volumes) was compared with four other inorganic reinforcing fillers in the same volume ratio: zinc oxide, gas black, prepared china clay, and colloidal barium sulfate. Rubber stocks compounded with mixtures of light magnesium carbonate with these same fillers, varying the proportions by regularly spaced increments, but maintaining the same total number of volumes of filler in each compound, were also studied. The third series included samples compounded with twenty volumes magnesium carbonate, with twenty volumes zinc oxide, and with various mixtures of these two fillers, having in each case a total of twenty volumes filler in the compound.

The materials used in the preparation of these rubber stocks were the best standard materials available in the market for use in rubber compounding, including zinc oxide of the highest quality, a superior grade of gas black, and impalpable sulfur. The china clay was a finely divided material especially prepared for rubber compounding and the colloidal barium sulfate was a high quality, highly dispersed product much superior to ordinary barytes. The magnesium carbonate was the ordinary light technical grade.

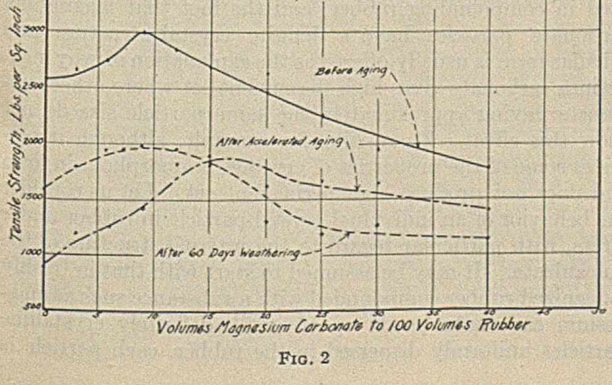

FIG. 2

PHYSICAL TESTS

The physical tests carried out upon all the samples discussed in this paper included:

TENSILE STRENGTH AND ULTIMATE ELONGATION—These values were obtained on a Scott testing machine using standard 0.25-in. width dumb-bell test strips. The results accepted as representing the actual values for these properties are in every case the average of the results from not less than five samples from the same sheet, the principle having been adopted of discarding results which were at great variance with the average and those in which premature failure of the test piece was obviously due to flaws in the sheet. Complete stress-strain curves for all the samples were obtained on the Scott testing machine, using two observers to secure the readings for the points on the curve.

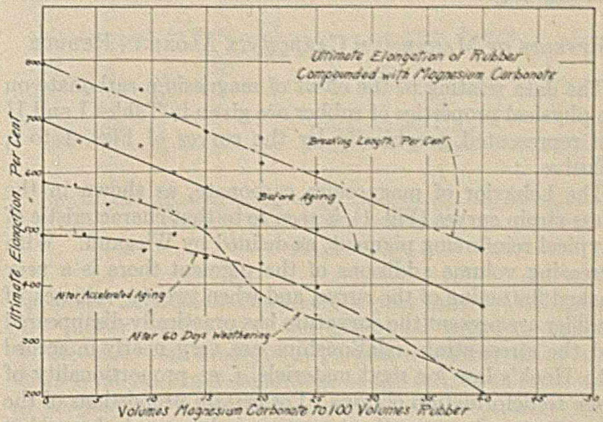

FIG. 3

TENSILE STRESS AT 300 PER CENT ELONGATION—The value for the load at 300 per cent elongation for each sample was obtained directly from the stress-strain curve plotted from the data obtained as just described.

TOTAL ENERGY OF RESILIENCE, AND ENERGY ABSORBED AT 300 PER CENT ELONGATION—Total energy of resilience was obtained according to the method of Wiegand, calculating from the area between the complete stress-strain curve and the elongation axis, and using a planimeter to determine this area. The energy absorbed by the rubber up to an elongation of 300 per cent was determined in the same way, using the planimeter to determine the area between the portion of the stress-strain curve below 300 per cent elongation, and the elongation axis.

PERMANENT SET—This property was determined by the method recommended by the Physical Testing Committee of the Rubber Division, using three stretches of the test piece to 60 per cent of the breaking length, with 5-min. rest intervals, and a final 10-min. rest before reading the permanent length deformation. The values given are the average of several tests on strips from the same sheet.

HARDNESS—The hardness of the samples was determined by means of a "durometer," a simple instrument depending on the penetration of a blunt point into the surface of the rubber sheet when a fixed pressure is applied. The range of hardness of vulcanized rubber is divided into an arbitrary scale, from "soft" at zero to "hard" at 100. The litharge-pale crepe basic mix used in this work gave a "durometer" hardness number varying from 40 to 42, depending upon the lot of rubber used. The hardness increases slowly with aging of the samples.

TENSILE PRODUCT—Calculated as tensile strength in lbs. per sq. in. multiplied by ultimate per cent length, and for convenience of numerical expression divided by 10,000.

ACCELERATED AGING TEST—All samples heated for 7 days at 71° C., in an oven through which a slow current of air was passing. This is considered to have approximately the same effect with respect to loss of tensile strength as 3.5 yrs.' aging under normal conditions.

WEATHERING TESTS—The samples subjected to this test were exposed to the atmosphere upon the roof of the building for 60 days during the summer months; this was a very severe test with respect to surface cracking tendencies and loss of tensile strength, and very few samples in the basic mix referred to above stood up well under this test.

TABLE I—DATA ON LIGHT MAGNESIUM CARBONATE

Volumes Light Magnesium Carbonate to 100 Vol. Rubber	Compound Composition by Weight—Per cent				Tensile Strength Lbs./Sq. In.	Tensile after Accelerated Aging Lbs./Sq. In.	Tensile after 60-Day Weathering Lbs./Sq. In.	Ultimate Elongation Per cent	Ult. Elong. after Accelerated Aging Per cent	Ult. Elong. after 60-Day Weathering Per cent	Permanent Set Per cent	Durometer Hardness Number
	Rubber	Sulfur	Litharge	Light Magnesium Carbonate								
0[1]	74.0	3.70	22.3	0	2575	872	1600	696	490	585	5.5	40
3	70.4	3.52	21.2	4.9	2670	1190	1815	658	488	580	10.0	46
6	67.1	3.36	20.2	9.5	2740	1280	1950	655	425	545	20.0	50
9	64.1	3.20	19.2	13.6	3000	1430	1980	655	460	550	23.0	52
12	61.3	3.06	18.4	17.3	2910	1810	1960	610	495	530	24.0	55
15	58.7	2.94	17.6	20.7	2700	1560	1910	575	450	505	28.0	58
20	54.9	2.74	16.5	25.8	2650	1620	1290	560	438	375	30.0	62
25	51.5	2.58	15.5	30.4	2280	1660	1200	500	396	345	29.0	66
30	48.6	2.43	14.6	34.3	1910	1590	1280	460	304	305	27.0	69
40	43.7	2.18	13.1	41.1	1770	1390	1130	363	200	230	23.0	74

[1] Basic mix.

EFFECTS OF MAGNESIUM CARBONATE ALONE IN RUBBER

The data relating to the effect of magnesium carbonate on the physical properties of rubber are given in Tables I and II and represented graphically by the curves of Figs. 1 to 7, inclusive.

The behavior of magnesium carbonate, as shown in the stress-strain curves (Fig. 1), is seen to be that characteristic of a typical reinforcing pigment, as defined by Wiegand. With increasing volume additions of the pigment there is a very marked flattening of the curve, and when twenty volumes of the filler are present the curvature has practically disappeared and the stress-strain relationships are very nearly in accord with Hook's law for rigid materials, *i. e.*, proportionality of stress to deformation obtains. For certain proportions of the filler the tensile strength at rupture is increased above that of the basic mix, while at the same time the ultimate elongation is considerably decreased.

The tensile strength curve (Fig. 2) shows that this property of the rubber is increased up to a maximum at nine volumes of the filler per one hundred of rubber, and then falls off rather uniformly, becoming equal to that of the basic mix at about twenty volumes per one hundred of rubber (see Table I). Nine volumes of the carbonate correspond to about twenty-one parts by weight. With another lot of rubber, samples have been prepared containing twenty-five volumes of magnesium carbonate in which the tensile strength is equal to that of the basic mix. The curve for tensile strength after accelerated aging shows that this basic mix, containing an excess of litharge, does not stand up well under the heat test, whereas the heavily compounded samples, containing large proportions of magnesium carbonate and less rubber, age better than the lightly compounded ones. The curve for tensile strength after the 60-day weathering test is of a different character and practically parallels the curve for tensile properties before aging. Compounds containing between six and twelve volumes of magnesium carbonate show the highest tensiles after this aging test.

Ultimate elongation values for the stocks of the above series are represented in Fig. 3. The falling off on the elongation with increasing volume additions of magnesium carbonate is shown to be very nearly linear, up to forty volumes per one hundred of rubber (see Table I). After accelerated aging the decrease in elongation with increasing proportions of the filler is found to be uniform, though not linear, the elongation of every stock being considerably less than before aging, corresponding to the decrease in tensile which results from the application of this heat test. The 60-day weathering test gave quite different results. The lightly compounded samples retained after weathering the greater part of their original elongation, while the heavily compounded samples were much stiffer after this test than before. This difference in stiffness and hardness was observable to the eye, without carrying out tensile and elongation tests, and the heavily compounded samples also showed some surface checking and cracking, while those compounded with smaller proportions of magnesium carbonate did not.

Fig. 4 illustrates the effects of rubber compounding materials on the hardness of rubber, comparing light magnesium carbonate with gas black, zinc oxide, and ordinary ground magnesite, the last named being a coarse pulverized natural magnesium carbonate which is not a reinforcing pigment. Magnesium carbonate gives rubber hardness very much greater than that given by ground magnesite, somewhat greater than that given by zinc oxide, but considerably less than that given by gas black, which produces very hard and rigid compounds, even when used in rather small proportions (Table I). It appears, therefore, that there is a relationship between the hardness of rubber compounded with a particular filler and the reinforcing and toughening effect of that filler, which may perhaps be expressed in terms of the slope of the curve showing increase of hardness with successive volume increments of filler. This curve seems to be linear only for inert or coarse fillers, and not for reinforcing pigments.

The permanent set figures for rubber compounded with magnesium carbonate, in comparison with ground magnesite, zinc oxide, and gas black, are represented in Fig. 5. Magnesium carbonate shows a rapid increase in permanent set with successive volume increments, up to twenty volumes per one hundred of rubber, and then a uniform decrease from the maximum value (Table I). This decrease is explained by the fact that the ultimate elongation values for the heavily compounded stocks are small and, therefore, a 60 per cent extension of these samples is a much smaller actual stretch than in the cases of the more lightly compounded samples having higher elongation, and gives, therefore, a smaller result for the permanent set figure. Magnesium carbonate gives much greater set effects than either zinc oxide or gas black and greater still than ground magnesite. The latter gave no set figure higher than 12.0 per cent even up to fifty volumes of this filler. This, it appears, is due to the fact that even with smaller proportions of the material the set effect is not very great, and with larger proportions the great decrease in the final elongation corresponding to the diluent effect of this inert filler, permits low permanent set values to be obtained by this method of making the test.

High permanent set is an effect which seems to characterize in a degree all definitely crystalline substances which are used in compounding rubber, and the fact that magnesium carbonate particles have a definite crystal structure and acicular form is usually offered as the explanation of why magnesium carbonate gives high permanent set where other substances having approximately the same particle size do not show this effect. Zinc oxide, for example, although it possesses some of the properties of crystals, is amorphous in form and does not produce high permanent set. Let us consider the behavior of an individual crystal particle in rubber under stress, with particular regard to the internal structure of the vulcanizate. It may be assumed to start with that in freshly vulcanized rubber compounded with a substance such as magnesium carbonate, made up of small, definitely crystalline particles uniformly dispersed in the rubber, each particle is in complete and uniform contact with the rubber matrix, *i. e.*, the rubber adheres closely to each crystal face. The particles will lie with their axes at various angles to the direction of applied stress in the sample and when this stress is increased until the elongation is sufficiently great, say 60 per cent, as in the permanent set test discussed above, there will be a tendency for the particles to align themselves with their long axes in the direction of the applied stress. Very powerful shearing forces will then come into operation, acting between the plane surfaces of the crystal lying parallel to the direction of stress, and the rubber matrix to which each crystal face is united by cohesion forces. These surface forces vary with the physical and chemical nature of the crystalline substance to which the rubber is bonded, and probably also with the presence of other substances dispersed or dissolved in the rubber. When the bonding between the particles and the rubber has been broken and the filler particles have reoriented themselves in the mass, the rubber can never completely return to its original conformation and the individual particles will never reunite themselves to the rubber in the same degree as they were when the rubber was first vulcanized.

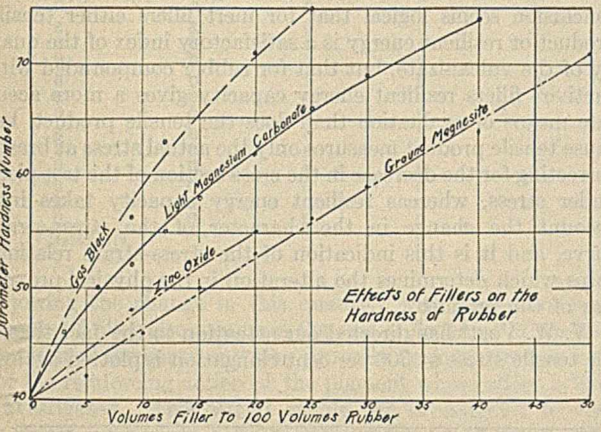

FIG. 4

Visible evidence of the separation of the magnesia particles from the rubber matrix may be obtained by stressing a sample cured with sulfur only. The sample will be practically translucent until blooming takes place, and when stretched there is a pronounced and permanent whitening, the result of the change in the refraction of the light passing through the rubber after the particles have become readjusted in the mass.

The behavior of an amorphous substance in rubber will be distinctly different, because the particles are irregular in surface contour and offer no plane surfaces to the rubber, which will, therefore, attach itself to the particle at many points of this irregular surface. The surface forces, therefore, instead of being exerted at plane surfaces and in one direction only, perpendicular to that surface, will be exerted in many directions, owing to the approximately spherical or irregular shape of the amorphous particle. Schippel[6] showed that compounded rubber when stressed gave an increase in volume, which he explained as being due to the formation of vacua at the poles of the particle in the direction of the applied stress. This was confirmed by Green,[7] who was able to show by examination of microsections of compounded rubber the actual formation of such vacua in rubber under strain, but his experiments indicated that no vacua were formed with fine pigments in rubber when compounded in small percentages.

Wiegand[8] directed attention to the fact that when a stock containing one of the "active" fillers is stressed to rupture, a part of the energy required goes toward distorting the rubber phase itself and a considerable part toward tearing apart the rubber matrix and the imbedded pigment particles. In the case of an amorphous particle in rubber under stress there is only a slight separation of the rubber to form vacua at the poles and since no plane surfaces are subjected to shearing stresses, there is not such a pronounced tendency for the rubber matrix to break its bonding to the individual particles, entirely aside from specific cohesion forces exerted between the rubber and the particle surface. Consequently there will not be a great tendency for the particles to change their orientation in the mass and give a volume increase and high permanent set. The conclusion seems unavoidable, therefore, that an amorphous light magnesium carbonate would give less permanent set than is obtained with the crystalline material manufactured by the present process, and the modification of the precipitation process to produce a material of less pronounced crystalline characteristics and, if possible, even smaller particle size is being made the object of considerable study at the Mellon Institute of Industrial Research. If this can be accomplished it should make light magnesium carbonate of much greater value to the rubber compounder, and the writer hopes to have the privilege of presenting some results of the work along this line at the next meeting of the Rubber Division.

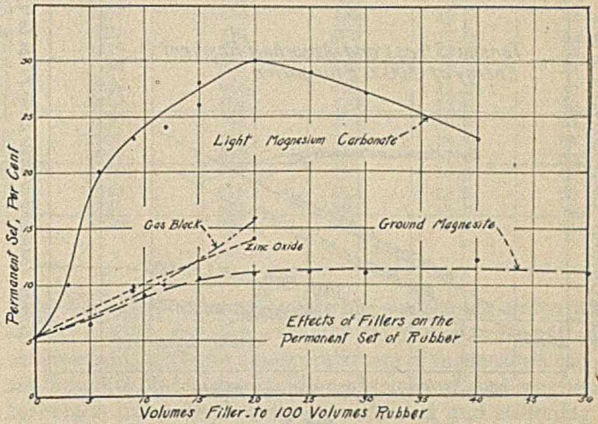

FIG. 5

Data representing the reinforcing effect of magnesium carbonate are shown in the tensile product and total resilient energy curves of Fig. 6. The tensile product values are not as high as those obtained by North, owing to the higher extensi-

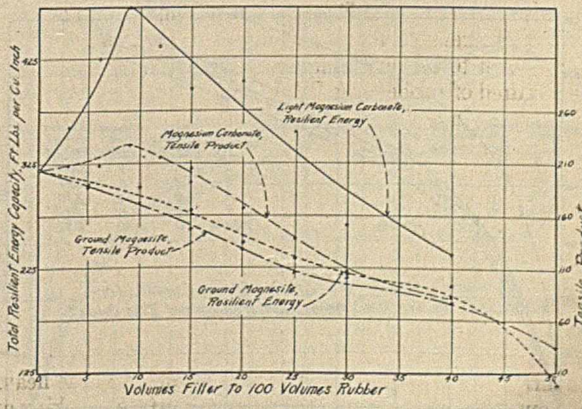

FIG. 6

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[6] THIS JOURNAL, 12 (1920), 33.

[7] *India Rubber World*, 65, (1922), 350.

THIS JOURNAL, 13 (1921), 118.

bility of the rubber-sulfur mix used in his work, as compared with that of this litharge-pale crepe mix. The curve has, however, approximately the same form. Tensile product reaches a maximum at nine volumes and becomes less than that of the basic mix at fifteen volumes; it is never very much greater than that of the basic mix. Quite different results are obtained with regard to resilient energy. (See Table II.)

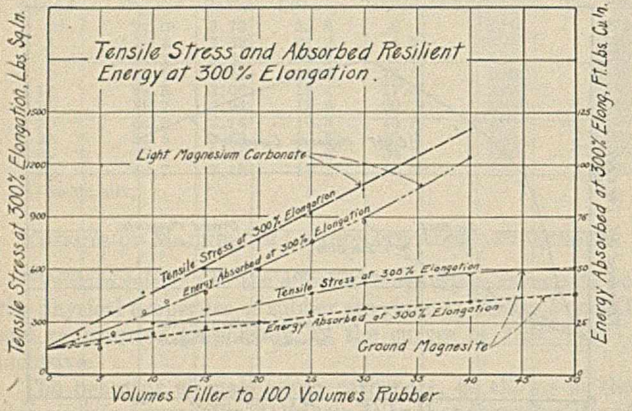

FIG. 7

TABLE II—DATA ON REINFORCING EFFECT OF LIGHT MAGNESIUM CARBONATE

Volumes Magnesium Carbonate to 100 Vol. Rubber	Tensile Product	Total Resilient Energy Ft. Lbs./Cu. In.	Resilient Energy Per cent of Base Mix Energy	Tensile Stress at 300 Per cent Elong. Lbs./Sq. In.	Energy Absorbed at 300 Per cent Elong. Ft. Lbs./Cu. In.
0	205	318	100	150	11.7
3	205	355	112	225	16.7
6	208	425	134	355	20.5
9	227	475	149	455	31.7
12	212	438	138	505	35.0
15	197	396	124	600	39.0
20	174	407	128	770	50.0
25	137	355	112	910	63.4
30	107	265	83	1050	71.3
40	82	233	73	1405	104.0

The maximum is reached at nine volumes, the same maximum as for tensile strength and tensile product, and the total resilient energy is then 49 per cent greater than that of the basic mix. Resilient energy capacity of the compounds does not become less than that of the basic mix until more than twenty-five volumes of magnesium carbonate are incorporated.

For comparison purposes, the tensile product and total resilient energy curves for rubber compounded with various proportions of ground magnesite have also been plotted. The two curves are found to be almost identical in form, and the plotted values for tensile product and resilient energy decrease uniformly with each successive addition of this inert filler, being in every case less than the values for the basic mix. This illustrates the difference in mechanical qualities between rubber compounded with reinforcing pigments and with inert fillers. From a study of these curves the conclusion seems logical that for inert fillers either tensile product or resilient energy is a satisfactory index of the quality of the vulcanizate, but that for rubber compounded with "active" fillers resilient energy capacity gives a more accurate means of evaluation than does the tensile product, because tensile product measures only the actual stress at break, correcting for the decrease in the cross section of the test piece under stress, whereas resilient energy capacity takes into account the change in the character of the stress-strain curve, and it is this indication of the stress-strain relationships which determines the alteration in the physical properties of the product.

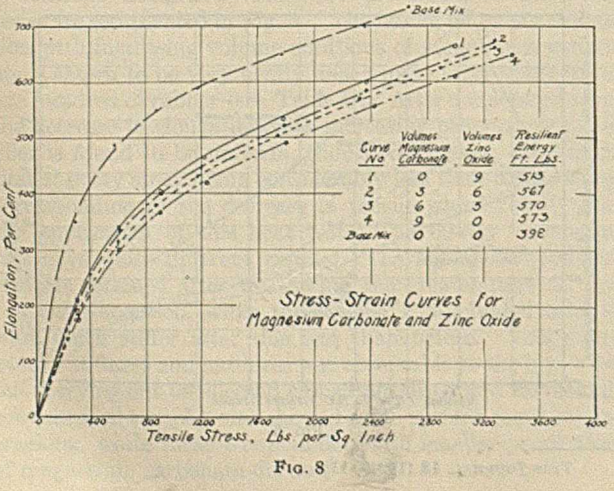

FIG. 8

W. W. Vogt[9] has directed our attention to the fact that if the tensile stress at 300 per cent elongation is plotted against the number of volumes of filler per one hundred volumes of rubber, the curve obtained is linear, showing an increase in load with increasing amounts of filler. The slope of this line, he concludes, is a measure of the stiffening or reinforcing action of the filler. On Fig. 7 will be found curves showing the relation between tensile stress at 300 per cent elongation for magnesium carbonate and for ground magnesite. The magnesium carbonate curve has a much greater slope than the ground magnesite curve, which is to be expected, corresponding to its greater reinforcing action. The slope of this line indicates the *rate of flattening* of the fore part of the stress-strain curve with increasing volume additions of the filler which is being studied. The magnesium carbonate curve is linear throughout and the ground magnesite curve is linear up to thirty volumes, and then flattens out somewhat.

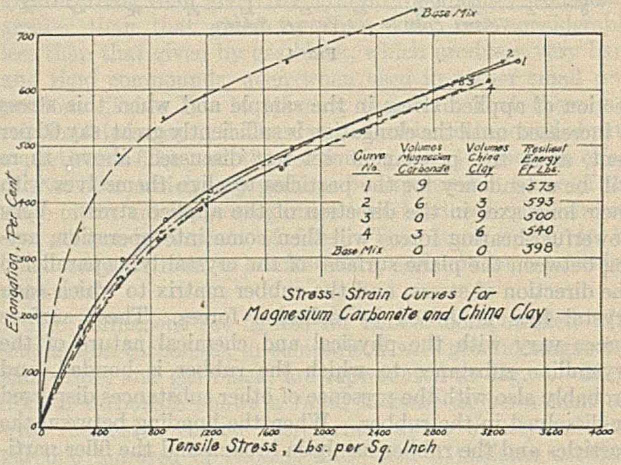

FIG. 9

On the same graph, for comparison purposes, there have been plotted the values for the resilient energy absorbed at 300 per cent elongation by rubber compounded with various proportions of light magnesium carbonate, and also with ground magnesite. The curves for absorbed energy at 300 per cent elongation are very similar in form to those just discussed above for tensile stress at 300 per cent elongation, although they are not perfectly linear. The spread between the absorbed energy curves for magnesium carbonate and ground magnesite is almost identical with that between the curves for tensile stress at 300 per cent elongation for the same fillers, and since the energy capacity of the rubber at 300 per cent elongation also depends upon the flattening of the fore part of the curve, the slope of the line

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[9] *India Rubber World*, **65** (1922), 347.

Table III—Data on Mixtures of Light Magnesium Carbonate with Other Reinforcing Pigments

Volumes Filler to 100 Volumes Rubber										
Magnesium Carbonate	Gas Black	Zinc Oxide	China Clay	Colloidal Barium Sulfate	Tensile Strength Lbs./Sq. In.	Tensile after Accelerated Aging Lbs./Sq. In.	Ultimate Elongation Per cent	Ult. Elong. after Accelerated Aging Per cent	Permanent Set Per cent	Durometer Hardness Number
0[1]	0	0	0	0	2650	1200	738	550	6.0	42
9	0	0	0	0	3400	2275	650	550	19.5	51
6	3	0	0	0	3440	2070	638	505	17.0	52
3	6	0	0	0	3600	1710	635	380	16.5	54
0	9	0	0	0	3450	1190	600	345	9.5	53
6	0	3	0	0	3290	2290	665	610	15.0	50
3	0	6	0	0	3285	2410	675	570	12.0	50
0	0	9	0	0	3000	1760	665	600	10.5	49
6	0	0	3	0	3300	2060	653	550	18.5	50
3	0	0	6	0	3200	2080	615	525	17.5	50
0	0	0	9	0	3000	1780	600	485	16.0	49
6	0	0	0	3	3075	2040	677	580	13.5	50
3	0	0	0	6	3020	1760	653	540	12.0	49
0	0	0	0	9	2810	1650	700	500	9.0	44

[1] Basic mix.

showing the change in this quantity with successive increments of filler also measures the *rate of flattening* of the lower portion of the curve and may properly be considered an index of the reinforcing action of the pigment whose effect is being investigated. This would enable the investigator to make a direct comparison between the reinforcing effects of different pigments on the basis of energy relationships rather than on tensile stress alone.

Comparison of Magnesium Carbonate with Other Reinforcing Pigments

Light magnesium carbonate gives its maximum reinforcing effect with respect to tensile strength, tensile product, and resilient energy capacity at nine volumes per one hundred of rubber. Magnesium carbonate was therefore compared at this volume ratio with equal proportions by volume of zinc oxide, gas black, prepared china clay, and colloidal barium sulfate. The effects of mixtures of magnesium carbonate with each of these fillers upon the physical properties were also studied, having a total of nine volumes filler in each compound, and varying by three-volume increments the proportions of magnesium carbonate and the other reinforcing pigments. These data, as given in Tables III and IV, and Figs. 8 to 18, inclusive, show in graphic form the changes in physical properties. It must be understood, of course, that nine volumes of the pigments other than magnesium carbonate do not represent the point of maximum reinforcement, which in the case of gas black, for example, is not reached until about twenty volumes are incorporated.

In Fig. 8 are represented the stress-strain curves for mixtures of magnesium carbonate and zinc oxide. Magnesium carbonate is shown to give a greater stiffening effect than zinc oxide in this volume ratio. The stress-strain curves of Fig. 9 for mixtures of magnesium carbonate and china clay show that magnesium carbonate has a stiffening action which is very slightly less than that of china clay. Fig. 10 gives stress-strain curves for similar mixtures of magnesium carbonate with colloidal barium sulfate, which show that magnesium carbonate has a much greater reinforcing and stiffening action than colloidal barium sulfate. Stress-strain curves for mixtures of magnesium carbonate and gas black are represented in Fig. 11. These show that gas black gives a stiffer rubber than magnesium carbonate, and that it has also a greater reinforcing action than china clay. In every case the mixtures of magnesium carbonate with the other reinforcing pigments give reinforcing effects intermediate between those obtained with either material in the same volume ratio alone, as shown by the relative positions of their stress-strain curves.

Tensile strength data for the compounds just discussed, represented by the curves of Fig. 12, show that magnesium carbonate compounded in the nine-volume ratio produces tensile strength somewhat greater than that given by zinc oxide or china clay in equal proportions, and considerably greater than that given by colloidal barium sulfate. The tensile with nine volumes magnesium carbonate is slightly less than that produced by nine volumes of gas black. The curve shows, and this has been confirmed by the preparation of several samples, that a mixture of six volumes gas black and three volumes magnesium carbonate per one hundred volumes of rubber gives a tensile value of 3600 lbs. per sq. in., considerably higher than can be obtained by the use of the same total volume of either filler alone in this basic mix. With the other reinforcing pigments, zinc oxide, china clay, and colloidal barium sulfate, there is a uniform falling off in tensile strength, with successive replacements of magnesium carbonate in the compound, by any one of these fillers (see data in Table III).

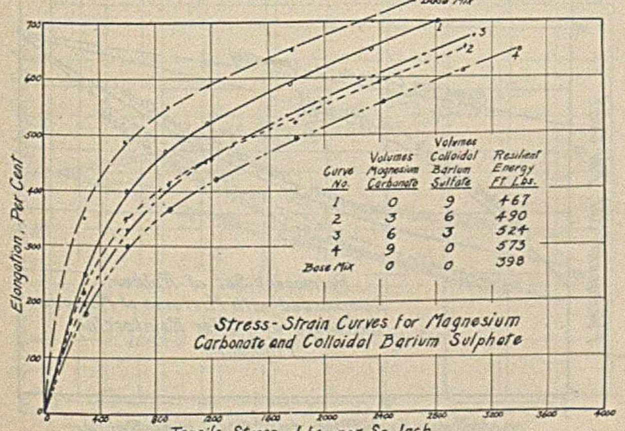

Fig. 10

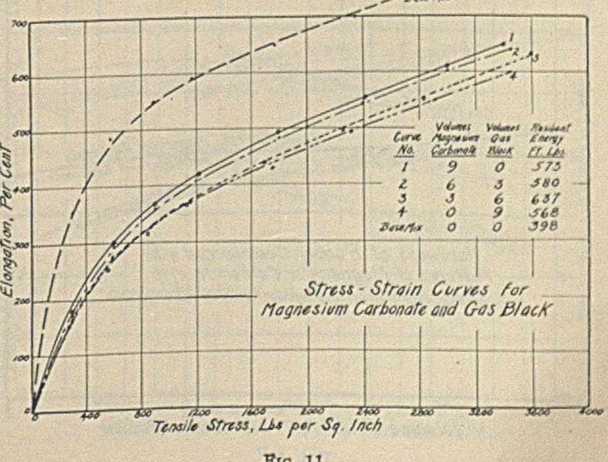

Fig. 11

Fig. 13 shows the loss in tensile strength of these compounds resulting from the accelerated aging test (data given in Table III). Inspection of the curves makes it evident that in this basic mix stocks containing gas black do not stand up well under this heat test. The best aging samples are those compounded with mixtures of zinc oxide and magnesium carbonate, although the stock containing zinc oxide alone loses a greater proportion of its original tensile strength. Samples compounded with colloidal barium sulfate, with china clay, with gas black, and with mixtures of magnesium carbonate with these other materials show poorer tensile values after accelerated aging than was the case with the compound containing only magnesium carbonate. In so far as this test may be considered of value in determining the aging qualities of compounded rubber, it is evident that magnesium carbonate compares very favorably with these other reinforcing pigments. The magnesium carbonate sample has lost 33 per cent of its original tensile strength, while the other compounding materials show losses of from 41 to 65 per cent.

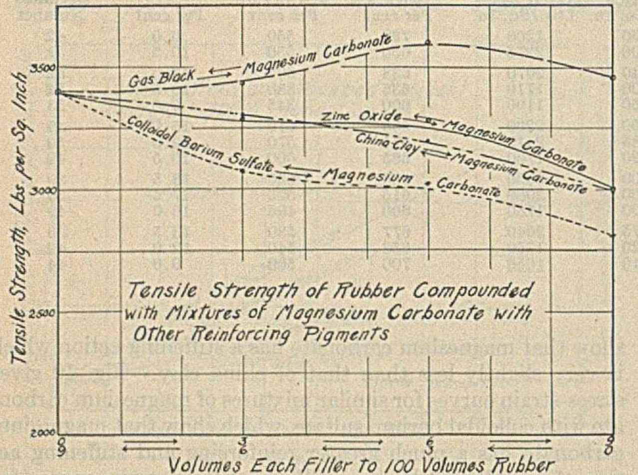

FIG. 12

The hardness of rubber compounded with mixtures of magnesium carbonate and these reinforcing pigments is shown by the curves in Fig. 14 (see data in Table III). In this volume ratio magnesium carbonate gives a vulcanizate slightly harder than is produced by the same proportion of either zinc oxide or china clay, and considerably harder than that given by the same volume of colloidal barium sulfate. This same volume of gas black gives a compound which is quite definitely harder than the magnesium carbonate compound.

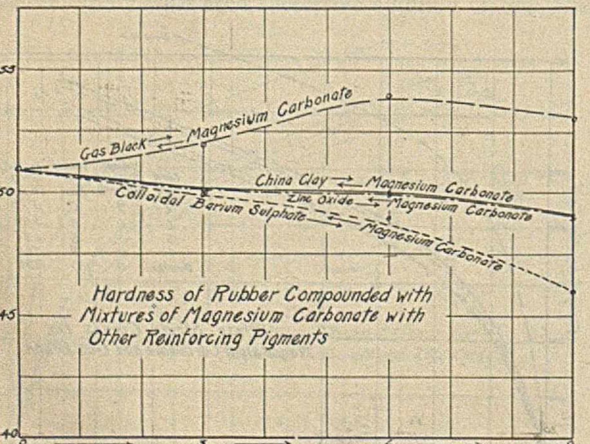

FIG. 14

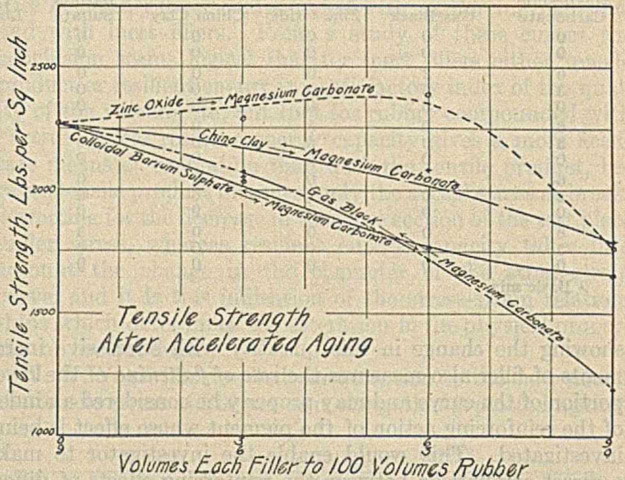

FIG. 13

Fig. 15 shows just the sort of results with respect to permanent set with mixtures of magnesium carbonate and other reinforcing pigments which would be anticipated from the preceding data and discussion of the permanent set effect given by magnesium carbonate, since these other fillers are all more amorphous than the carbonate. The set with mixtures of china clay and magnesium carbonate increases almost linearly with increasing proportions of magnesium carbonate, although clay itself produces rather high permanent set. In the case of mixtures of gas black and magnesium carbonate the set increases more rapidly than in a linear ratio. The permanent set of the compound previously referred to, containing six volumes gas black and three of magnesium carbonate, is 17.5 per cent. It should be remarked that the compound containing nine volumes of carbonate, although it has a greater tensile strength than was given by the same volume of this filler in the other lot of pale crepe used in the preliminary study of its effect, gives a lower permanent set, only 19.5 per cent, as compared with 23.0 per cent.

The rate of increase in permanent set in the compounds containing mixtures of magnesium carbonate with zinc oxide and with colloidal barium sulfate is seen to be less than that corresponding to a linear ratio.

The resilient energy capacity curves, Fig. 16, show some interesting results. Magnesium carbonate shows higher resilient energy in this volume ratio than zinc oxide, china clay,

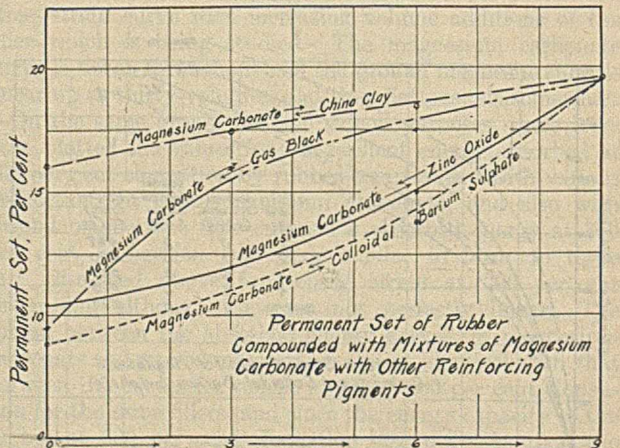

FIG. 15

Table IV—Data on Reinforcing Effects of Mixtures of Magnesium Carbonate and Other Reinforcing Fillers

Volumes Filler to 100 Volumes Rubber: Light Magnesium Carbonate	Gas Black	Zinc Oxide	China Clay	Colloidal Barum Sulfate	Tensile Product	Total Resilient Energy Capacity Ft. Lbs./Cu. In.	Resilient Energy Per cent of Basic Mix Energy	Tensile Stress at 300 Per cent Elongation Lbs./Sq. In.	Energy Absorbed at 300 Per cent Elong. Ft. Lbs./Cu. In.
0[1]	0	0	0	0	222	398	100	200	25
9	0	0	0	0	255	573	144	600	68
6	3	0	0	0	253	580	146	650	70
3	6	0	0	0	265	637	160	715	77
0	9	0	0	0	242	568	142	775	80
6	0	3	0	0	252	570	143	565	62
3	0	6	0	0	255	567	142	525	57
0	0	9	0	0	230	513	129	490	52
6	0	0	3	0	248	593	149	650	73
3	0	0	6	0	228	540	136	700	71
0	0	0	9	0	210	500	126	745	79
6	0	0	0	3	239	524	132	515	57
3	0	0	0	6	228	490	123	465	50
0	0	0	0	9	225	467	117	380	44

[1] Basic mix.

Table V—Data on Mixtures of Light Magnesium Carbonate with Zinc Oxide

Volumes Filler to 100 Volumes Rubber: Light Magnesium Carbonate	Zinc Oxide	Gas Black	Tensile Strength Lbs./Sq. In.	Tensile after Accelerated Aging Lbs./Sq. In.	Tensile after 60-Day Weathering Lbs./Sq. In.	Ultimate Elongation Per cent	Ult. Elong. after Accelerated Aging Per cent	Ult. Elong. after 60-Day Weathering Per cent	Permanent Set Per cent	Durometer. Hardness Number
0[1]	0	0	2650	1200	1780	738	562	530	6.0	42
20	0	0	2890	1720	1290	560	460	413	28.0	64
15	5	0	2950	1720	1270	580	415	425	24.0	60
11	9	0	2830	1860	1540	585	463	494	15.0	58
7	13	0	2780	1730	1730	600	448	522	14.0	57
3	17	0	2840	1890	1970	595	500	535	16.0	56
0	20	0	2820	1760	1870	615	520	545	12.0	55
0	0	20	3950	1580	..	490	230	..	16.5	70

[1] Basic mix.

or colloidal barium sulfate, and equal to that of gas black. The high resilient energy values obtained with this proportion of magnesium carbonate are explained by the fact that this material gives high tensile strength, high elongation, and a pronounced flattening of the stress-strain curve; therefore the area between the curve and the elongation axis is large and the calculated resilient energy is correspondingly great. The compound previously noted, containing six volumes gas black and three of magnesium carbonate, which gives high tensile strength, is also found to give the highest resilient energy value, 637 ft. lbs., or 60 per cent increase above the energy of the basic mix (see data in Table IV).

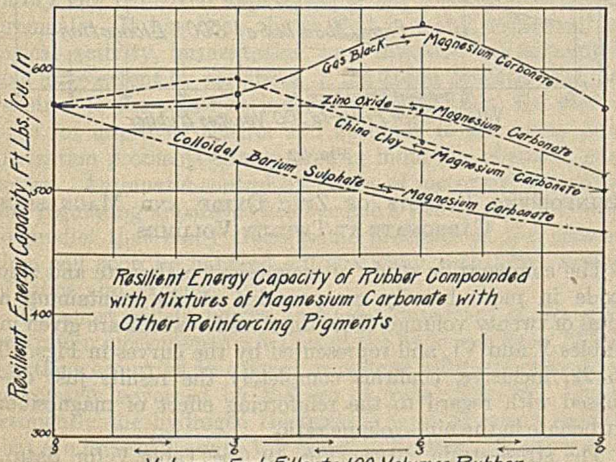

Fig. 16

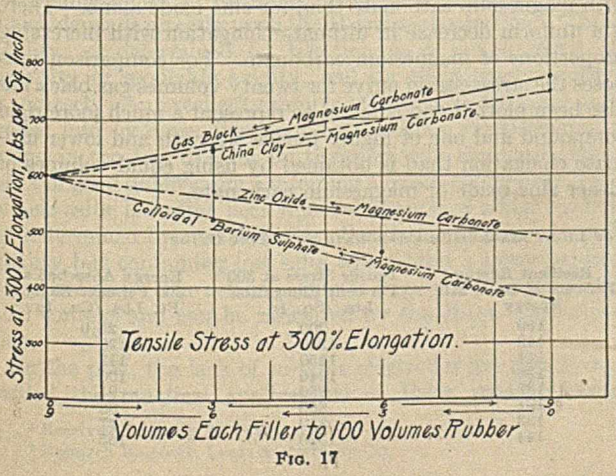

Fig. 17

A comparison of the stiffening effect produced by magnesium carbonate and the other reinforcing pigments studied, on the basis of tensile stress at 300 per cent elongation, is given in Fig. 17 (based on data in Table IV). The curves representing tensile stress at 300 per cent elongation are all linear, for these mixtures of reinforcing pigments, and with respect to stiffening effect at this volume ratio of each filler, would place them in the following order of increasing reinforcing power: colloidal barium sulfate, zinc oxide, magnesium carbonate, china clay, gas black.

Fig. 18 gives curves for energy absorbed at 300 per cent elongation, making possible a direct comparison of these mixtures of magnesium carbonate with other reinforcing pigments, on the basis of energy values rather than on tensiles alone. The curves, it will be seen, lie in about the same relative positions and have approximately the same spread,

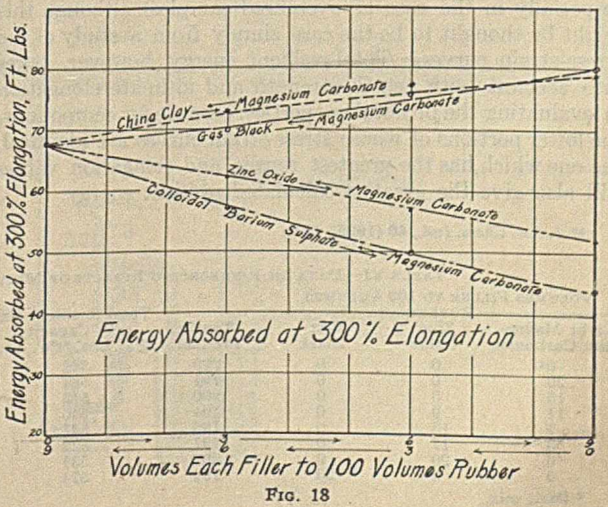

Fig. 18

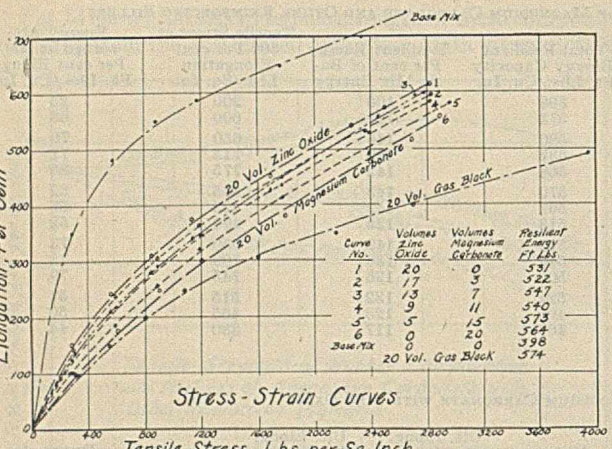

FIG. 19

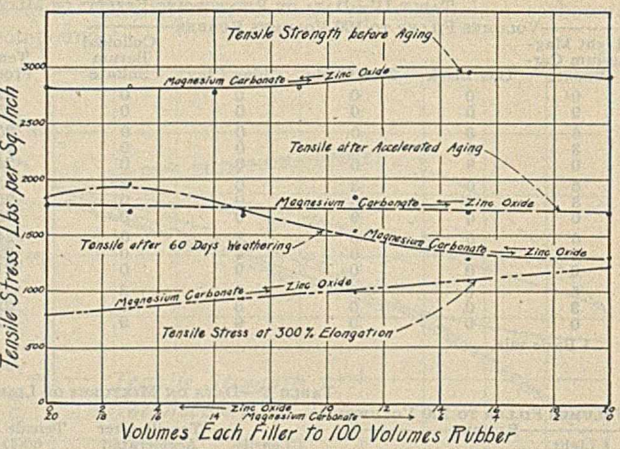

FIG. 20

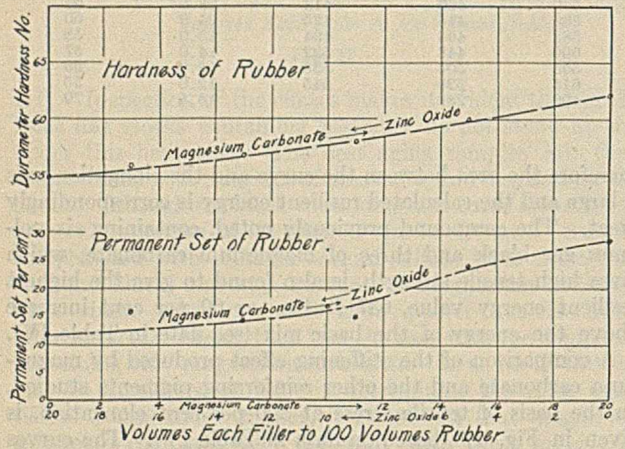

FIG. 21

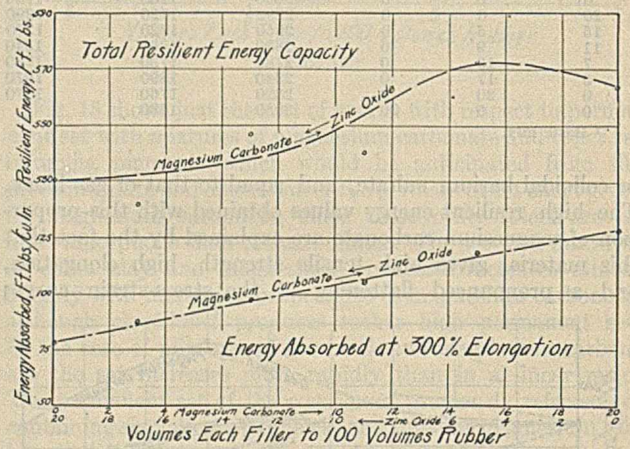

FIG. 22

but are not exactly linear. The order of increasing reinforcing power in the rubber is the same as given above for tensile stress at 300 per cent elongation, except that gas black and china clay are more nearly equal. (See Table IV.) It should be remarked, however, that this comparison takes into account only the stiffening effect on the fore part of the stress-strain curve and does not express the fact that higher tensile strength and total energy values are given by gas black and magnesium carbonate than can be obtained with clay. Schidrowitz and Burnand[10] have pointed out, also, that great rigidity is not always associated with toughness (especially in the case of overcured samples) although this might be thought to be the case simply from a study of the stress-strain curves. Total resilient energy, however, takes into account both tensile strength and ultimate elongation in evaluating the physical properties, because for compounds, the lower portions of whose stress-strain curves are identical, the one which has the greatest tensile and elongation values will also give the greatest calculated resilient energy.

REINFORCING EFFECTS OF ZINC OXIDE AND MAGNESIUM CARBONATE AT TWENTY VOLUMES

The comparative study of magnesium carbonate and zinc oxide in more heavily compounded stocks, containing a total of twenty volumes filler, the data for which are given in Tables V and VI, and represented by the curves in Figs. 19 to 22, inclusive, confirms completely the results just discussed with regard to the reinforcing effect of magnesium carbonate in the nine-volume ratio.

The stress-strain curves, Fig. 19 (see Table V for data), show considerably greater stiffness for magnesium carbonate and for the compounds containing mixtures of zinc oxide with magnesium carbonate than for zinc oxide alone. There is a uniform decrease in ultimate elongation with increasing proportions of magnesium carbonate. For comparison purposes the stress-strain curve for twenty volumes gas black has also been plotted and is found to represent a much more rigid compound and one of higher tensile strength and lower ultimate elongation than is obtained by using equal volumes of either zinc oxide or magnesium carbonate.

TABLE VI—DATA ON REINFORCING EFFECTS OF MIXTURES OF LIGHT MAGNESIUM CARBONATE WITH ZINC OXIDE

VOLUMES FILLER TO 100 VOLUMES RUBBER							
Light Magnesium Carbonate	Zinc Oxide	Gas Black	Tensile Product	Total Resilient Energy Capacity Ft. Lbs./Cu. In.	Resilient Energy Per cent of Basic Mix Energy	Tensile Stress at 300 Per cent Elongation Lbs./Sq. In.	Energy Absorbed at 300 Per cent Elong. Ft. Lbs./Cu. In.
0[1]	0	0	222	398	100	200	25.0
20	0	0	191	564	142	1230	128
15	5	0	200	573	144	1150	113
11	9	0	194	540	136	1040	100
7	13	0	195	547	137	980	95
3	17	0	197	522	131	860	88
0	20	0	202	531	133	810	77
0	0	20	194	574	144	1520	155

[1] Basic mix.

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[10] *J. Soc. Chem. Ind.*, **40** (1922), 268*t*.

The tensile strength curves, Fig. 20, show values for this property which are nearly the same for all the compounds, probably within the experimental error due to slight differences in the state of cure. The same is true of the tensile values after accelerated aging. After the 60-day weathering test, however, it is observed that the stocks containing the larger proportions of zinc oxide show definitely better aging qualities than those containing larger proportions of magnesium carbonate, as a result of the greater surface cracking tendency of rubber heavily compounded with magnesium carbonate. This again seems to be related in a degree to the crystalline character of the magnesium carbonate particles, since the plane surfaces and sharp edges of the crystals would be expected to favor the development of cleavage planes in the rubber itself when stressed, or perhaps even under the influence of changes in temperature, producing alternate expansion and contraction of the rubber matrix around each particle.

The hardness and permanent set (Fig. 21) of these compounds both show increasing values with increasing proportions of magnesium carbonate. The permanent set, however, does not exceed 16 per cent until half the zinc oxide has been replaced by magnesium carbonate.

The total resilient energy capacity and energy absorbed at 300 per cent elongation (Fig. 22 based on data in Table VI) both show a marked increase with successive increments of magnesium carbonate replacing zinc oxide in the compound. For the absorbed energy at 300 per cent elongation this increase is linear, as is also true of the curve showing stress at 300 per cent elongation for the same compounds (Fig. 20).

The Application of Ion Concentration Measurements to the Control of Industrial Processes[1]

By Earl A. Keeler[2]

Leeds & Northrup Co., Philadelphia, Pennsylvania

THE significance of ion concentrations has been the subject of many investigations during the last few years. The results obtained have demonstrated without question the unlimited possibilities existing for laboratory and industrial application of ion concentration measurements. It has been shown that in many instances biological activity, fermentation, and filtration are influenced to a large extent by variations in the H-ion concentration, or reaction of the solutions involved. In addition, the way is open for improved control and accuracy in the many neutralization problems encountered in industrial chemical processes. Automatic control by means of motor driven valves and regulating apparatus has become a reality, and it is safe to predict that many troublesome problems of the present time will soon be handled automatically with great saving of labor and expense.

The most widely known and most important of ion concentration measurements is that of the hydrogen ion. Many reactions occurring in colored or opaque solutions cannot be adequately governed by the use of color indicator. Quite frequently the hydrogen electrode is used to secure results that are impossible with the use of indicators. Another important asset lies in the ability of the hydrogen electrode to distinguish between actual acidity and total acidity. The controlling factor in reactions is usually the actual acidity, which depends directly upon the H-ion concentration. Total acidity, as determined by titration, is a measurement of quantity or available acidity, and its effect upon reaction is indirect. An excellent example of the errors that one may be led into by depending upon total acidity measurement is found in the test of milk by titration with standard alkali. Milk of good quality, but containing a relatively large amount of acid salts, has often been rejected because of a high acidity as determined by titration. Another batch of milk of equal quality but containing less salts will exhibit a lower acidity when titrated. The actual acidity is largely due to the lactic acid content and can be measured by the H-ion concentration.

In the past, the lack of suitable electrodes has greatly retarded the practical applications of H-ion measurements to plant industrial problems. Fig. 1 shows a typical laboratory set-up consisting of a hydrogen electrode and a calomel electrode connected into a potentiometer circuit. One can readily realize the difficulties that would be encountered in applying such structures, or even radical modifications, to plant work. The calomel electrode at its best has often been a troublesome affair for unskilled hands to handle, and the hydrogen electrodes have lacked the requirement of convenient and rapid change of electrode surfaces. Contamination of hydrogen electrodes is usually unavoidable in most industrial processes. For this reason it is extremely important that the electrode elements may be easily removed and replaced.

Several new electrodes which are well suited for industrial work have been recently developed. These electrodes are shown in section in Fig. 2. It is to be noted that the structures are practically unbreakable, there being no glass parts used. The hydrogen electrode element is a disk of platinum gauze held in position by a knurled ring of hard rubber. A fresh electrode disk may be substituted for a used disk inside

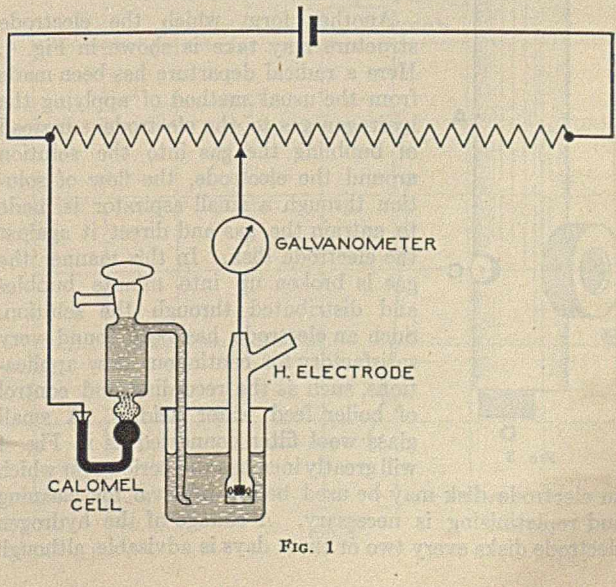

Fig. 1

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[1] Received February 24, 1922.

[2] Research Engineer, Leeds & Northrup Co.

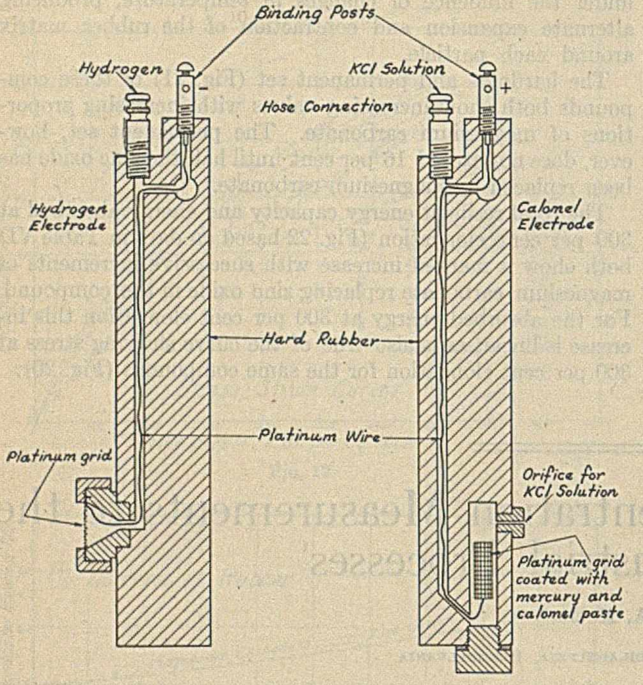

FIG. 2

of one minute. The calomel electrode is also unbreakable and contains no loose mercury. By coating a platinum grid with a paste of mercury and calomel, an electrode is secured that can be shipped ready for use. The only requirement is that a reservoir of potassium chloride solution be connected to supply the small flow of potassium chloride necessary to prevent diffusion of the solution under test into the calomel electrode. Fig. 3 shows the electrodes of Fig. 2 combined into one structure. The terminals, or binding posts, are shown at E and F. G and H are the connections for hydrogen and the potassium chloride solution. The knurled ring holding the hydrogen electrode disk is shown at B. The orifice of the calomel electrode is the removable plug C. The knurled end plug D closes the calomel electrode chamber into which the paste-coated grid is mounted. The main body of the combined electrode, A, is made of hard rubber.

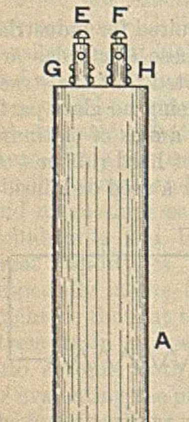

FIG. 3

Another form which the electrode structure may take is shown in Fig. 4. Here a radical departure has been made from the usual method of applying the hydrogen gas to the electrode. Instead of bubbling the gas into the solution around the electrode, the flow of solution through a small aspirator is made to entrain the gas and direct it against the electrode disk. In this manner the gas is broken up into minute bubbles and distributed through the solution. Such an electrode has been found very satisfactory for continuous flow applications, such as the recording and control of boiler feed water acidity. A small glass wool filter connected as in Fig. 4 will greatly increase the period over which an electrode disk may be used before removal for cleaning and replatinizing is necessary. A change of the hydrogen electrode disks every two or three days is advisable, although experience has shown that such electrode will sometimes operate satisfactorily for several weeks without cleaning.

The hydrogen-ion method is particularly well adapted to the control of neutralization processes and the measurement of low acidity or alkalinity. Fig. 5 shows a reproduction of a record produced by an automatic hydrogen-ion recorder during the reaction of sodium hydroxide solution with hydrochloric acid solution. It will be noted that the greatest change of voltage for a given change in acidity takes place around the neutral point. The ordinate of this record is marked "time" and may be taken as proportional to change of acidity or alkalinity. The records shown in Figs. 6, 7, 8, 9, and 10 are typical of the results that are secured upon application of the hydrogen-ion recorder to many industrial problems.

The carbonation of beetsugar juice is shown in the record of Fig. 6. Milk of lime had been added to this juice prior to the carbonation. It will be noted that the curve is practically flat (1.05 volts) during the first portion of the carbonation. Then a break occurs, producing a "knee" in the curve. During the remainder of the carbonation the slope of the curve is very appreciable, thus giving considerable change in voltage for small changes in alkalinity. Three samples were taken between the "knee" of the curve and the neutral point. The titration of these samples was made with $0.036\,N$ sulfuric acid and the results expressed in grains of calcium oxide per 100 cc. of solution. Phenolphthalein was used as an indicator.

Fig. 7 shows the record secured during the neutralization of pineapple juice. Milk of lime is added to the juice until the neutral point is reached. Phenolphthalein tests showed that 0.75 volt corresponded to the real neutral point.

An interesting application of the recorder is shown in Fig. 8. The changes of alkalinity occurring when tooth paste goes into water solution are of importance because of the necessity for proper neutralization of the reaction known as "acid

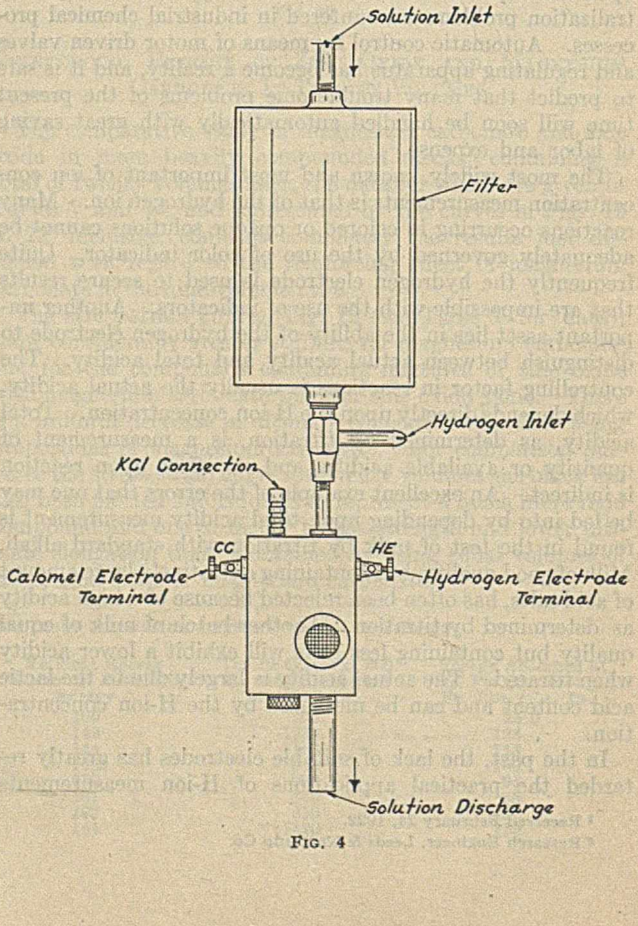

FIG. 4

mouth." The shape of the curve shows that the alkalinity becomes practically constant after the first 2 or 3 minutes.

A peculiar record is reproduced in Fig. 9. The alkalinity of wool scouring liquor is difficult to determine because of the color and suspended matter of all kinds. A titration of some of this liquor with sulfuric acid resulted in the record of Fig. 9. The liquor contains some free alkali in the form of soda ash, some soap made up of red oil, soda ash, and the solution constituents of the greasy wool containing complex organic acids combined with potash. It seems that there are three steps involved in the neutralization: (1) the neutralization of the free alkali; (2) the decomposition of the red oil soaps; and (3) the liberation of a gas caused by the decomposition of the potash-organic acid compounds.

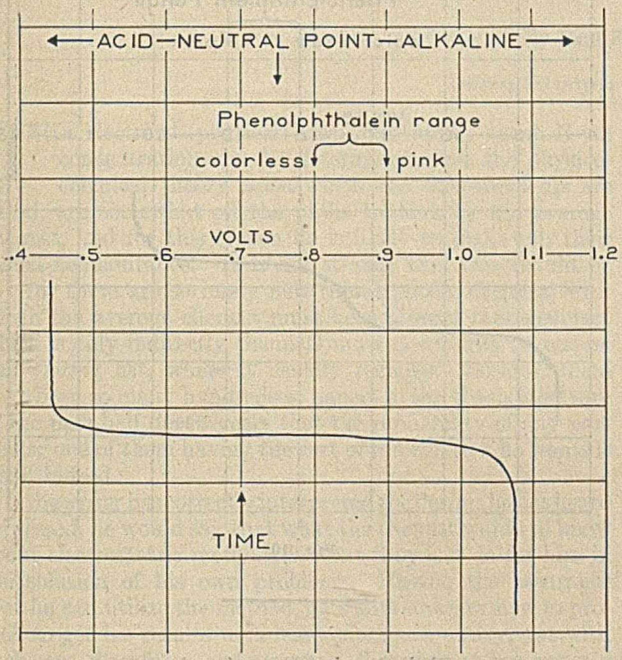

Fig. 5

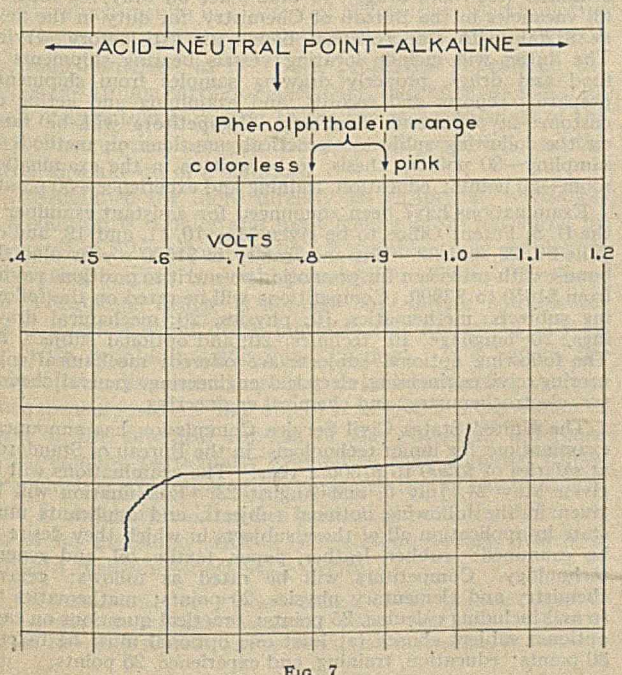

Fig. 7

Another interesting feature is shown in Fig. 10, and here the two end-points of the reaction of phosphoric acid with sodium hydroxide indicate the formation of the primary and secondary phosphates.

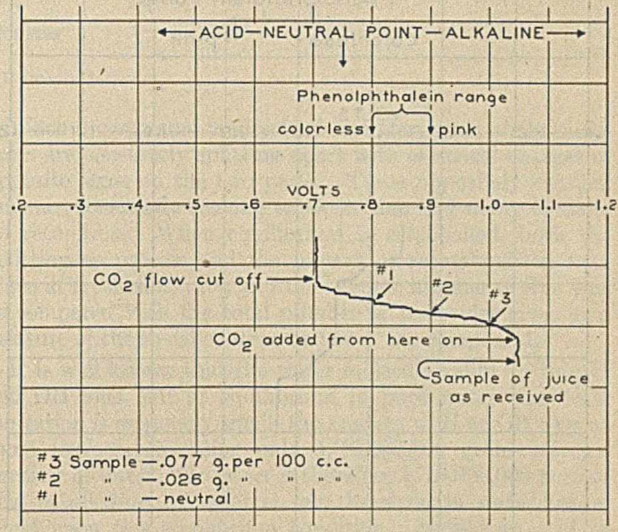

Fig. 6

These are only representative of the many possibilities existing for the application of ion concentration methods. Several comprehensive papers have recently been published on the subject of H-ion measurements as applied to filtration problems in water purification[3] and sewage disposal.[4] Another subject upon which a great deal of interesting work has been done, is that concerning the effect of the hydrogen-ion concentration upon the properties of tanning liquors used in the leather industry.[5]

The step from recording apparatus, such as that shown in Fig. 11, to equipment for automatic control is a natural one to undertake. Frequently, the advantages to be gained by automatic control are far greater than those secured by re-

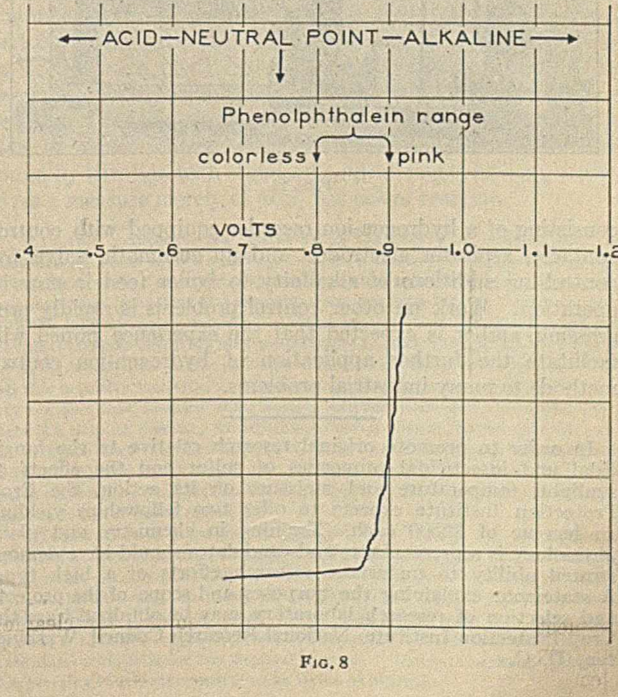

Fig. 8

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[3] Abel Wolmand and Frank Harman, *Chem. Met. Eng.*, **25** (1921), 502.

[4] J. A. Wilson and H. M. Heisig, This Journal, **13** (1921), 406.

[5] J. A. Wilson and Erwin J. Kern, *Ibid.*, **13** (1921), 1025.

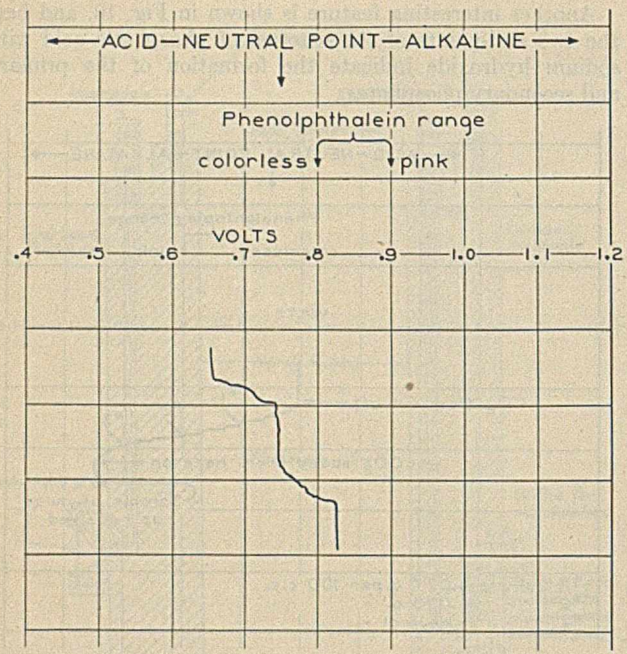

Fig. 9

cording alone. An illustration of such a condition is found in the requirements for efficient operation of boilers in a modern power plant. It is known that the hydrogen-ion concentration, or actual acidity of boiler feed, is one of the factors upon which the corrosion of a steam boiler and its auxiliaries depends. Maintenance of feed water at a slight alkalinity usually reduces corrosion to a minimum. An installation consisting of a hydrogen-ion recorder equipped with control contacts, aspirator electrodes, and an automatic valve for controlling additions of alkalinity to boiler feed is now in operation. Work on other control problems is rapidly progressing, and it is expected that the experience gained will facilitate the further application of hydrogen-ion control methods to many industrial problems.

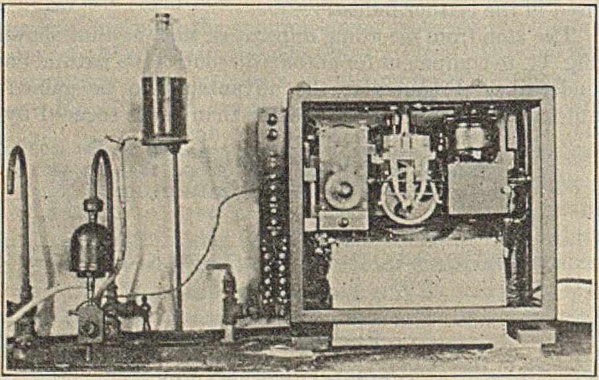

Fig. 11

In order to promote original research relative to the fungicidal and insecticidal properties of sulfur and the effects of sunlight, temperature and moisture on its action, the Crop Protection Institute expects to offer two fellowships yielding an income of $2500 each. Training in chemistry and plant physiology is a prerequisite, and candidates should have demonstrated ability to undertake research efforts of a high type. A statement explaining the purposes and scope of the projects and selection of research laboratory may be obtained from the Crop Protection Institute, National Research Council, Washington, D. C.

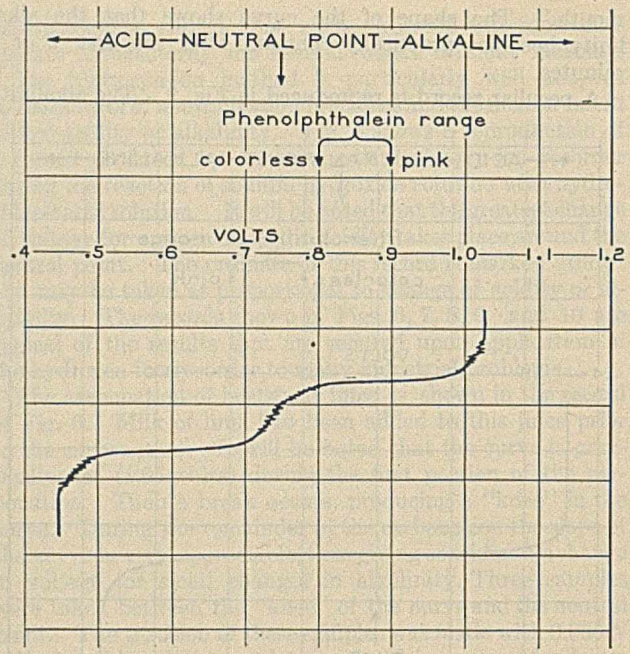

Fig. 10

Civil Service Examinations

The United States Civil Service Commission has announced an examination for associate chemist at $2500 to $3600 a year and assistant chemist at $1800 to $2500 a year, applications to be rated as received until further notice. Applicants must qualify in one of the following branches of chemistry: advanced inorganic, analytical, biological, dairy, explosives, food, fuel, metallurgical, organic, pharmaceutical, physical, soil, petroleum, gas, ceramic. Applicants will be rated on education, training and experience—70 points, publications or thesis (to be filed with application)—30 points. While applications for examination in all of the fifteen optional subjects are desired, there is particular need for eligibles qualified in the chemistry of explosives.

An examination has also been announced for junior wharf examiner (food and drugs), to take place on May 10, 1922, to fill vacancies in the Bureau of Chemistry, for duty in the field, at $1200, with Congressional bonus for satisfactory service. The duties will include locating vessels bearing shipments of food and drugs, properly drawing samples from shipments, preparing reports and records, and examining and acting on customs invoices and manifests. Competitors will be rated on the following subjects: practical questions on methods of sampling—30 points; thesis, to be written in the examination room—20 points; education, training and experience—50 points.

Examinations have been announced for assistant examiner in the U. S. Patent Office, to be given May 10, 11, and 12, and on June 21, 22, and 23. Entrance salary is $1500 a year plus the bonus, with provision for promotion on merit to positions paying from $1650 to $3900. Competitions will be rated on the following subjects: methematics, 10; physics, 20; mechanical drawings, 20; language, 10; technics, 20; and optional subject, 20. The following optional subjects are offered: mechanical engineering, civil engineering, electrical engineering, general chemistry, electrochemistry, and chemical engineering.

The United States Civil Service Commission has announced examinations for junior technologist in the Bureau of Standards, at salaries of $1200 to $1500 a year. The examinations will be given May 24, July 5, and August 23. Examination will be given in the following optional subjects, and applicants must state in application all of these subjects in which they desire to be examined: rubber, leather, paper, textile, oil, and general technology. Competitors will be rated as follows: general chemistry and elementary physics, 20 points; mathematics up to and including calculus, 25 points; practical questions on each optional subject chosen (at least one optional must be taken), 30 points; education, training, and experience, 25 points.

Some Practical Aspects of Hydrogen Electrode Measurements[1]

By Paul E. Klopsteg[2]

Central Scientific Co., Chicago, Illinois

The electrical (physical) measurements by which H-ion concentration can be determined, and the physicochemical theory upon which the measurements are based, are somewhat off the paths trodden by the average chemist, and for this reason he is likely to make only their casual acquaintance. It is not strange that this should be so; for there are so many new things purely chemical with which the average chemist must keep abreast that a subject which is only indirectly chemical must necessarily be put on the waiting list, where it usually remains. Besides, there have been so many hundreds of papers in the H-ion literature of the past half dozen years that the probability of any particular one of them having the sort of information he wants is small indeed.

If the writer has correctly interpreted the desires he has heard expressed, he would say that what the chemist wants to know about electrometric methods is what they can do for him in the solution of his own problems. Having the assurance that he can utilize the method, he wants to know how to proceed to get his results with least effort and outlay, yet with such ease, directness, and accuracy, that the net balance is a saving of time and money. This paper is an endeavor to answer these questions as accurately as possible; or, where a definite answer cannot be given, to point out the reason, and to suggest the best procedure for finding the answer.

Electrical methods of measurement and control in chemistry are possible because of the essentially electrical nature of the mechanism of a chemical reaction, *i. e.*, of the ions involved in the reaction. There are two distinctly different electrical properties of solutions that can be used to produce or control mechanical effects in a manner corresponding to chemical changes in the solution. These are, first, *conductance*, the property of a solution which permits an electric current to pass more or less freely. The second is the characteristic which results in a *potential difference* or electromotive force being set up between the solution and an appropriate electrode immersed in it. Both properties depend on the ion, or the atomic carrier of electricity, and no great strain on one's imagination is needed to see the reasonableness of the very close relation between the electrical properties and the chemical make-up of a solution.

Conductance (or more directly its reciprocal, *resistance*) of a solution is usually and most conveniently measured by means of a Wheatstone bridge of suitable type, employing alternating current to avoid polarization effects. However, the Wheatstone bridge is not the only device suitable for the purpose—several other methods well known in physics can, with suitable modifications, be used. It is beyond the limits of this discussion to go into details concerning conductance measurements. My object is to give a presentation of some of the practical aspects of the potential difference measurements, particularly applied to that potential difference which is a function of the concentration of the hydrogen ion. It should be said at this point that potential difference *cannot* be measured with a Wheatstone bridge, which is purely a resistance-measuring device.

When a compound is dissolved in water, some of its molecules are constantly splitting apart with electrical charges of opposite signs on the two parts. These oppositely charged ions are constantly seeking to recombine and many of them do recombine. When equilibrium is established, both the splitting-up process and the process of recombination take place at a constant rate, and the average number of free ions as compared with the total number of molecules gives us a measure of the so-called dissociation of the compound.

It is well known that the water molecule splits up into H and OH ions, but at equilibrium in pure water the total ionization is extremely small, the amount of H or OH ions at room temperature being only 1/10,000,000 gram-molecule per liter of water; the water is therefore 1/10,000,000 normal acid *or* alkaline. A neutral salt dissolved in water has no effect upon this equilibrium condition. Should an acid or base be put into the water, however, the former increases the number of H ions and the latter the number of OH ions, with the result that the rate of combination of oppositely charged ions becomes greater, and when equilibrium is established, the concentration[3] of H and OH ions, respectively, will be much greater than 1/10,000,000 normal.[4] With an acid like HCl, for example, it is easily possible to have such a high degree of ionization that in a molar solution of HCl, more than 80 per cent of the hydrogen is ionized. Such an acid, in which a relatively large proportion of the H atoms are ionized, is regarded as a strong acid. The strength of an acid is thus related to the number of H ions present in the solution. If, for example, a molar solution of acetic acid be made up, only 4.3 parts per thousand of the available hydrogen will be ionized. Bases behave similarly with respect to OH-ion concentration. These considerations bring out the distinction between *available* and *actual* hydrogen- or hydroxyl-ion concentration. In both HCl and CH_3COOH, the molar solution contains available hydrogen to the extent of 1.008 g. per liter; but in the first instance there is present in ionized form, ready to react, about 0.83 g., while in the second there are only 4.3 mg. Measurements of H-ion concentration involve a direct determination of the concentration of *actual* ionized hydrogen present. This cannot be found by titration with standard neutralizing solutions, which gives a measure merely of *total*, not *actual* reaction.

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[1] Presented before the Chicago Section of the American Chemical Society, October 21, 1921; before the South Bend and Mishawaka Section, November 22, 1921; and before the Indiana Section, December 9, 1921.

[2] Manager of Development and Manufacturing

[3] In this connection the writer takes the liberty of quoting from a statement he made several years ago in L. & N. Catalog No. 75, footnote, p. 6: "The discrepancies observed, especially in strong acids, between the ionic concentrations as measured by conductivity methods on the one hand and with the hydrogen electrode on the other, suggest that the quantity which we call H-ion concentration may not actually represent the degree of normality of hydrogen ions in the solution under test. Some have preferred to call this quantity 'activity.' Whatever name we choose to apply to it, the fact remains that in connection with a solution containing hydrogen ions there is a definite quantity susceptible to measurement, to the different values of which there correspond very definite characteristics of the solution. In this discussion we prefer to use the term 'hydrogen-ion concentration,' and in so doing we shall feel no concern regarding the objections which have been made to the use of the term."

[4] This fraction is more simply expressed as 1×10^{-7}, the negative exponent of 10 signifying that the power of 10 indicated is the denominator of the fraction. It is evident that any value between 1/10,000,000 and 1/1,000,000, the latter being the same as 10/10,000,000, can be expressed by a factor between 1 and 10, times 10^{-7}. The factor need not be purely integral, *i. e.*, it may be an integer plus a fraction, *e. g.*, 6.43×10^{-7}. The same statements hold for any decimal interval. This is the common method of expressing H-ion concentrations in terms of normal.

It is important to observe that, whatever the H-ion concentration may be when a substance is dissolved in water, the product of the concentration of H and OH ions is 10^{-14}. Hence, in designating acidity or alkalinity, it is merely necessary to mention the value of H-ion concentration, for its OH-ion concentration follows directly from this figure as shown a moment ago. Another point worth remembering is that, when the H-ion concentration is 10^{-14}, the OH-ion concentration is 10^0, or normal.

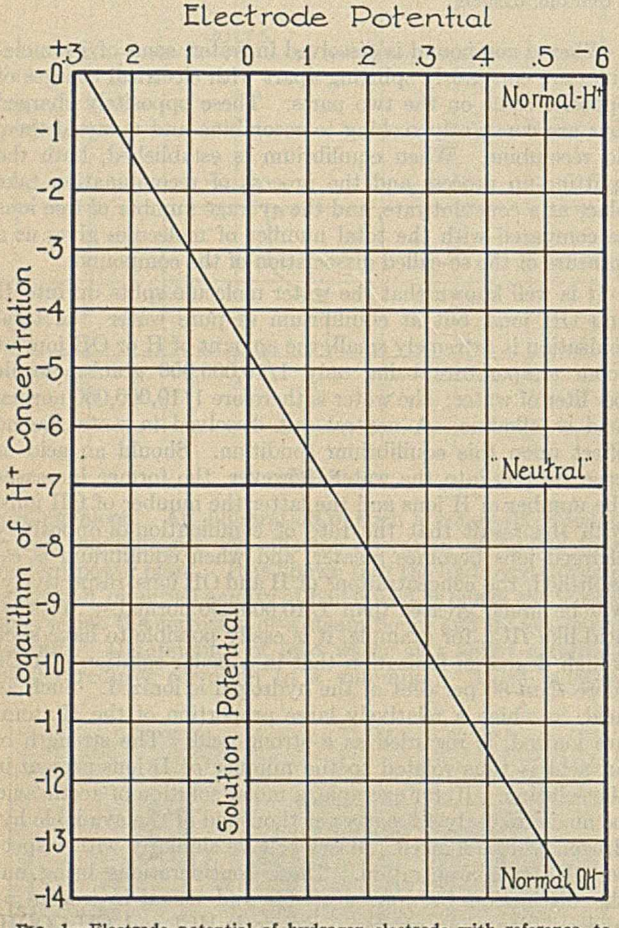

Fig. 1—Electrode potential of hydrogen electrode with reference to solution in which it is immersed, plotted against logarithm of hydrogen-ion concentration.

If we put an electrode of any metal or of hydrogen into a solution containing the corresponding ions, there will be set up, as a result of establishment of equilibrium between the solution pressure of the electrode substance and the osmotic pressure of the ions, a potential difference between the electrode and the solution. You will recall that potential difference (measured in volts or millivolts), sometimes called voltage, bears to electricity exactly the same relation that pressure bears to water. The higher the water pressure, the greater will be the speed with which a given quantity of water passes any point in a pipe or the greater the current. Similarly, the greater the potential difference, or electric pressure, the stronger the electric current resulting when a path is provided in which it may flow. But just as water pressure can exist statically, without causing a current of water, *e. g.*, when the pipe is stopped, so a potential difference can exist without causing a current, *e. g.*, when no circuit is provided. And it is this electrical pressure or voltage which varies as the concentration of the ions varies. It may be positive or negative with reference to the solution, *i. e.*, may have a deficiency or excess of electrons as compared with the solution, this depending on the solution pressure of the metal and the osmotic pressure or concentration of the ions of that metal.

The measured values of H-ion concentration, whether they be determined colorimetrically or by the methods which are here being discussed, derive their status from Nernst's equation,

$$E = E_0 + \frac{RT}{nF} \log_e C^+,$$

in which E is the potential difference between an electrode and the solution containing the corresponding ions; E_0 is the electrolytic potential, or the particular value of E when the ionic concentration C^+ in the solution is normal; R is the gas constant; T, the absolute temperature; *n*, the valence of the ion; F, the faraday, or 96,500 coulombs; and $\log_e C^+$ is the natural logarithm of the ionic concentration.

Taking the hydrogen electrode specifically, this is nothing more than a coating of platinum black deposited on an inactive metal, and exposed sufficiently long to a hydrogen atmosphere to become saturated. Such an electrode is positive to the solution when the concentration of hydrogen ions is normal; zero, when the concentration is somewhat less than 1/100,000; and is negative for lower values of concentration. This is shown in Fig. 1, which is a graph of Nernst's equation as applied to the hydrogen electrode. The values of potential used are based on observations, recorded in chemical literature, made with the dropping electrode or upon the curvature of the mercury surface in the tube of a capillary electrometer. They are approximately correct, probably within 10 millivolts. These potential values are plotted as abscissas, and the common logarithm of the concentration as ordinates. We have here adopted the convention of plotting the curve in the fourth quadrant, so that decreasing actual acidity is represented by a downward slope of the graph. This is also consistent with the fact that the logarithms are negative, since C^+ for hydrogen is always expressed as a fraction of normal, and the logarithm of a fraction is a negative number. On this scale of ordinates, -1 means 0.1 *N;* -2 means 0.01 *N*, etc., since $\log 1/10 = -1$ and $\log 1/100 = -2$. This scale, taken positively, is called the pH scale,[5] according to Sörenson's suggestion. Because of its convenience, biochemists have unanimously adopted the pH scale.

To convert a pH number[6] to actual H-ion concentration it is necessary only to find the number corresponding to the

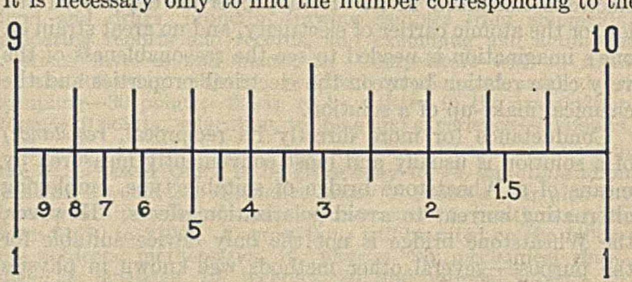

Fig. 2—Showing use of slide rule for converting pH into C^+ and vice versa. Upper scale represents scale of equal parts (whole length of rule) and lower scale the inverted logarithmic scale.

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[5] Properly written, this should be p_H, the derivation being that the number is proportional to the potential of the H electrode. For convenience in typographical work, pH is quite generally used.

[6] It is unfortunate that a single method for designating acidity and alkalinity has not been adopted. There are arguments for both the pH system and the numerical designation of H-ion concentration. The former, which is not as commonly used among chemists as the latter, has the advantage that pH values are linearly proportional to voltage, and the worker soon associates the pH value with perfectly definite characteristics of a solution. The latter, though it has definite physical meaning and is therefore more logical to use, is somewhat cumbersome, and greater effort is required to become fluent in its use.

pH value taken as a negative logarithm. As an illustration of this conversion process, suppose we wish to determine the H-ion concentration of a solution whose pH number is 9.54. The logarithm of the concentration sought is -9.54. The negative sign means that the corresponding value is a *fraction*, the denominator of which is the number whose logarithm is 9.54, or the fraction of normal concentration is 1/3,500,000,000. This mode of expression is awkward. A better way is to write it in accordance with the plan mentioned in Footnote 3, or $\frac{1}{0.35} \times 10^{-10}$, which is 2.88×10^{-10}.

Conversion from pH to C and vice versa is easily made with a slide rule having a scale of reciprocals, or with an ordinary slide rule, by inverting the slide. The scale of equal parts then reads the portion of the pH number after the decimal point, while the inverted scale reads the concentration factor which is multiplied by 10 with a negative exponent greater by 1 than the characteristic (preceding the decimal point) of the pH number. Fig. 2 will serve as a guide in following this example on a slide rule.

We now have the following picture: An electrode of platinum black, saturated with hydrogen, in a solution; a potential difference between the electrode and the solution, depending upon the H-ion concentration. The problem is to measure this potential difference and its variations as the concentration of H ions changes. To make the measurement with an electrical measuring instrument requires that means be found to connect the instrument to the electrode and solution, respectively, without introducing any additional potential differences into the circuit which, in the measurement, could not be differentiated from the potential difference we are trying to measure. We could make a metallic connection to the hydrogen electrodes, which would result in no difficulty; but how shall we connect to the solution and not run into trouble? Obviously we cannot use a metal electrode, dipping it into the solution, for this would be the seat of an unknown variable electromotive force. But a liquid junction can be established at which the e. m. f. is either negligible or very small and determinable; and if we can hold the second liquid invariable, and immerse in it a suitable electrode connected to our apparatus, the answer might be found. Although this would almost surely introduce an e. m. f. in series with the significant e. m. f., the former would be constant and determinable.

An obvious thought is to use as the second liquid, through which connection to the test solution is established, a solution of fixed H-ion concentration, in combination with a second hydrogen electrode. This gives us a connection such that the over-all potential difference will be measurable, and in which any variation of potential is due only to the changing H-ion concentration in the test solution. Fig. 3 illustrates the idea.

The same arrangement of electrodes, with the addition of a galvanometer and tapping keys with protective resistance, as shown in Fig. 4, serves a very useful purpose[7]—that of enabling the user to adjust the pH of a solution to be very closely the same as that of another reference or standard solution. Consider A and F immersed in solutions of different pH values, assuming B to be more acid than D. The electrical pressure (potential difference) is such that A tends to cause a flow into B; at the same time F tends to cause a flow of electricity into D, but the pressure is not so great, since D is less acid. If the circuit be closed through the galvanometer, a current flows, and causes a deflection, because of these unbalanced tendencies. Now let us imagine that B is a solution of exactly the proper acidity, and that we wish to render D as nearly like B as possible. All we need to do is to add H ions to D until the galvanometer shows no deflection when the key is closed. This method requires no knowledge of units—only of manipulation. An illustration would be to use a salt solution in B, and to titrate the corresponding acid with the corresponding base in D. Or, we might put a solution of known H-ion concentration in B, and use the arrangement in lieu of the more usual color indicator. This method has found much application in the adjustment of bacteriological culture media. Each end-point, of course, requires a particular solution of known pH value. By this and the other electrometric methods to be described, it is easily possible to titrate to within 0.01 pH unit. This is far closer than we can work with the best color indicators under the most favorable conditions.

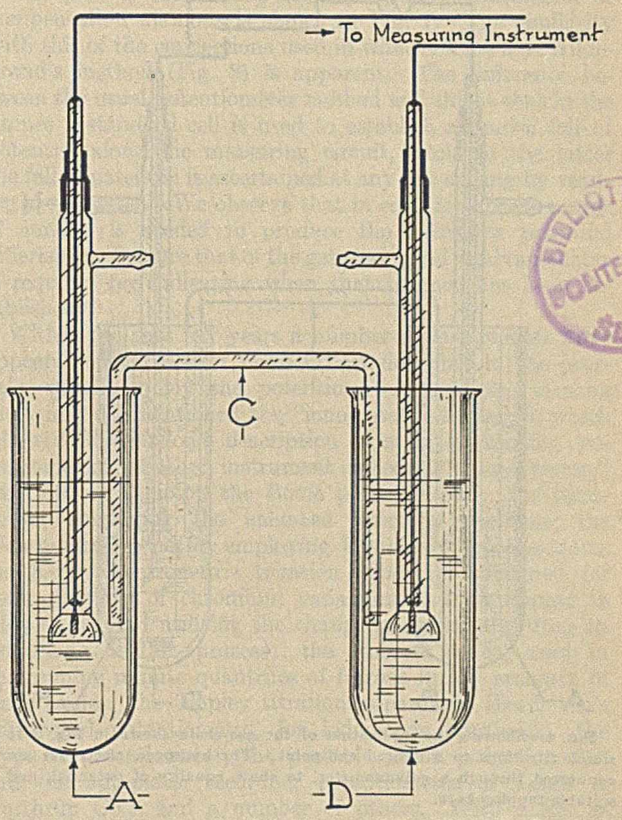

Fig. 3—A possible "gas-chain" arrangement, in which A is the standard solution, D the test solution and C the connecting tube. The latter is filled with a neutral conducting liquid, like KCl; the ends are plugged with cotton wool to prevent diffusion. The hydrogen electrode potential in A remains fixed, while that in D varies with the acidity of D.

The simplicity of application of color indicators makes them a very useful tool in the chemist's kit. As to the limits of their usefulness, we might say in general that turbidity or color in solutions, poor lighting conditions, and some kinds of salts and proteins make accurate determinations difficult, and when such conditions are encountered, the chemist should be on his guard lest he assume that he is getting greater accuracy than is actually the case. With a clear and colorless solution serving as the vehicle for a simple, well-defined reaction, we can expect an absolute accuracy of ±0.3 pH unit or slightly better. For many purposes this is ample, since, at the equivalent point of a titration, a few drops suffice to change the concentration of the H and OH ions by several pH units. The result is that in a simple titration with strongly ionized reagents almost any one of the usual indicators, such as methyl orange, phenolphthalein,

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[7] The arrangement and the application here described were suggested by the writer in *Science*, N. S., **52** (1920), 18, where a more complete description may be found.

azolitmin, and many others investigated by different workers, give a sufficiently accurate indication of the neutral point.

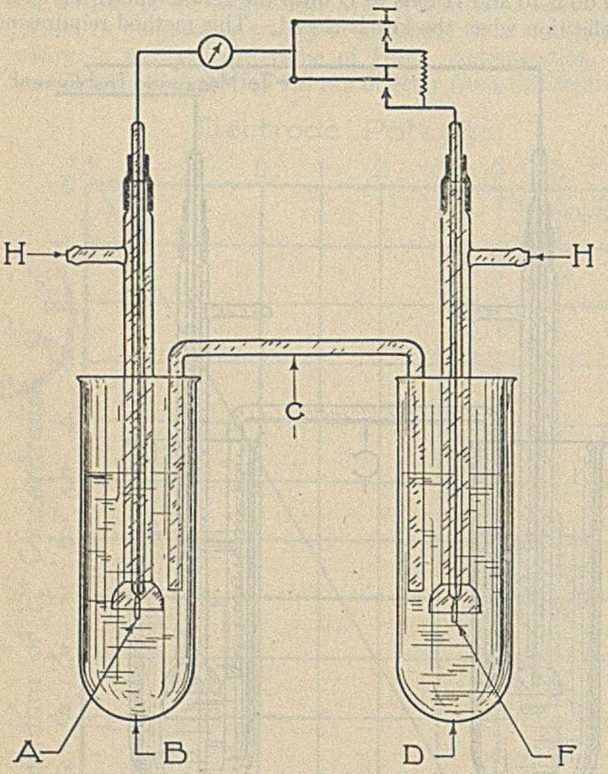

FIG. 4—Showing the application of the gas chain shown in Fig. 3 to simple titrations to a desired end-point. The hydrogen electrodes are connected through a galvanometer, to show equality of potential, and suitable tapping keys.

If, however, we desire to adjust an acidity or alkalinity in a particular region where there is no sudden change, it is necessary to be careful in the selection of the indicator, which should change color rapidly in the region in which we are interested. Methyl red, for example, could not be used as an indicator outside the limits 4.5 to 6. Another important point to observe is that all indicator ranges have been established with the hydrogen electrode, and that the color indicator is a secondary rather than a primary method in analysis or control. We may make the summary that the electrometric method is superior to the colorimetric method in the fact that with it we may often secure information that would be impossible to obtain by the indicator methods; and that in any case to which the hydrogen electrode can be applied, the results will be much more accurate than with an indicator. Where the color indicator methods can be used, they are to be recommended for their convenience.

Both the colorimetric and electrometric methods can to good advantage employ solutions of known pH, for check tests if for no other reason. Sörenson, Clark and Lubs, and others have worked out formulas for so-called "buffer mixtures" of any desired pH value. The "buffer mixture" is a mixture, such as an acetate, phthalate, or phosphate, which has great stability as regards changes in pH. For example, although very careful experiments show pure water to have an H-ion concentration of 10^{-7}, measurement on distilled water of high purity will seldom yield this value, because even the slightest acid or alkaline contamination (*e. g.*, carbon dioxide from the air) may change this exceedingly small concentration tenfold or a hundredfold. We can, however, produce a stable solution having a concentration of 10^{-7} by mixing 50 cc. of 0.2 *M* KH_2PO_4 with 31 cc. of the same strength NaOH, and diluting to 200 cc. Specific application of such a solution has already been indicated in the comparison method of titration, employing only a galvanometer.

Returning from this brief digression to the question of how to find quantitatively the variation in potential of the hydrogen electrode with reference to the test solution, we have seen that an electrode of fixed and determinable potential in an unvarying solution can be added to the chain, and that it affords a means for access to the quantity to be measured. Any such auxiliary electrode will do; but the type which has come into most general use, and which is generally accepted as the most satisfactory and convenient is the so-called calomel half-cell, or "calomel electrode." It has a variety of modifications in design and execution. Essentially it consists of pure mercury as the electrode proper, covered with a layer of pure calomel in solution of potassium chloride of known saturation, which itself has been saturated with calomel. The cell with 0.1 *N* KCl has probably been most closely studied; but there are certain advantages in the use of a more concentrated potassium chloride solution, which will be pointed out later. The cell has a side arm, or siphon tube, through which connection is established with the solution under test. Quite commonly, where accurate measurements are desired, a "connecting vessel" is used, containing saturated potassium chloride solution. This is interposed between the test solution and the calomel electrode for the purpose of eliminating liquid contact potentials. Since the latter seldom exceed a few millivolts, the connecting vessel can, in most practical work, be omitted. The common arrangement, known as a "gas chain," is shown in Fig. 5.

With an arrangement of this kind, we know that a certain potential difference exists between the mercury and the hydrogen electrodes, and that to any particular potential difference there corresponds one particular value of H-ion concentration. If we assume for the moment that this potential difference can be measured, we can apply our working formulas,

$$V = v - 0.0591 \log C^+,$$

or, since $pH = -\log C^+$,

$$V = v + 0.0591\ pH,$$

to the determination of either C^+ or pH. The formulas come directly from Nernst's equation, which has previously been explained. In them V is the measured voltage, and *v* is the voltage which would be measured if the hydrogen electrode were in a solution having normal concentration of hydrogen ions; for in such a solution $C^+ = 1$, $\log 1 = 0$; hence $pH = 0$. Fig. 6 clearly illustrates the formulas. In this figure length

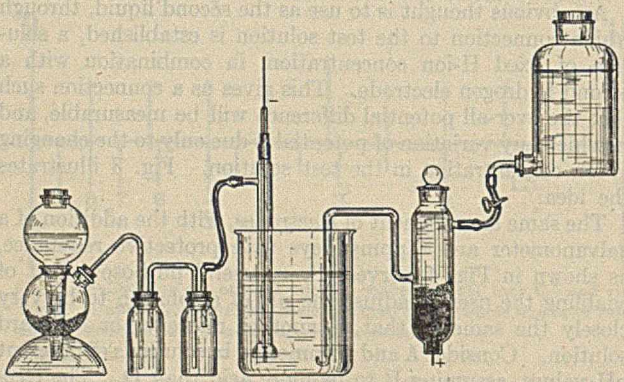

Fig. 5—Sketch of commonly used gas chain, showing hydrogen electrode supplied with hydrogen from Kipp generator, purified in wash bottles; calomel electrode with rubber tube connection to stock solution of KCl. Both electrodes in electrical contact with solution under test in beaker.

of line is proportional to voltage; AD represents the measured voltage, and AB the voltage which would exist between the calomel electrode and a hydrogen electrode in a solution of normal H-ion concentration. AO represents what is known as the electrode potential of the calomel electrode (0.560 volt at 18° C. for a 1.0 *N* KCl solution) although it is to be noted that this does not enter into our computations. The portion BD of the line corresponds to an abscissa in Fig. 1, O in the latter corresponding to the point O in Fig. 6.

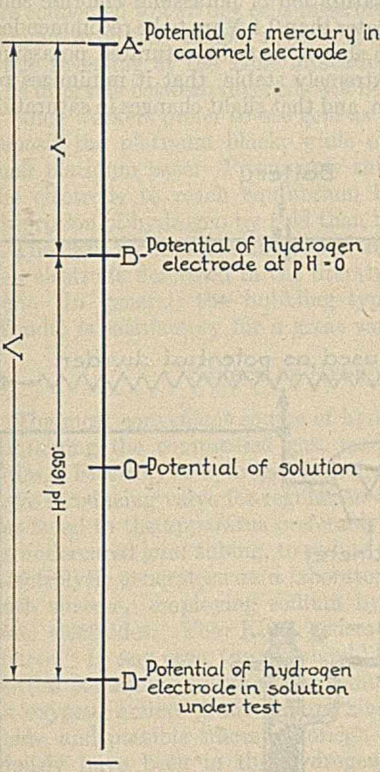

Fig. 6—Diagrammatic representation of relative potentials of calomel and hydrogen electrodes, and solution potential. This gives a graphic illustration of the working formula for the type of gas chain shown in Fig 5.

A very important practical question now is how to measure the voltage between the hydrogen electrode and the calomel cell. The hydrogen electrode is said to be in equilibrium when, on further exposure to hydrogen gas, its potential does not change in an unchanging solution. As has been stated, the calomel electrode has merely the unchanging reference potential, which may be likened to a fixed point with reference to sea level, from which we measure the electrical level of the hydrogen electrode. We find that to make this measurement accurately we must draw no current from the hydrogen electrode, for to do this would change its potential. We may compare it with a standpipe of small diameter, the level of the water in which changes if ever so little water be drawn off. Our problem in measurement of this voltage between hydrogen and calomel electrodes—in other words, of the gas chain—then resolves into this: It must be measured without permitting any appreciable flow of electricity through the electrodes.

In physics we have three methods, which have long been well known, for accomplishing this purpose. These are, first, the electrometer, of the quadrant type, which is relatively unimportant in this discussion; second, and also of small importance, the charging of a condenser by connection to the gas chain, and measuring the charge with a so-called ballistic galvanometer; the third and really important method is that employing a means for balancing a measurable, adjustable, potential difference against the unknown. To return to the analogy which has been used several times in this presentation, it may be likened to some such scheme of measuring the pressure of water in a standpipe by using a second standpipe in which the head, and hence the pressure, is adjustable and measurable, and "bucking" the second against the first. If, on opening the valve connecting the two pipes, there is no flow in either direction, as shown by a flowmeter, the two pressures are equal, and the first is known, since it is equal to the second which is measurable.

Potentiometer Methods

The plan of connections underlying all potentiometer or compensation methods is shown in Fig. 7. The similarity with this of the connections used in what is known as Hildebrand's method (Fig. 8) is apparent. The difference between the usual potentiometer method and this is that in the former a standard cell is used to establish a known fall of potential along the measuring circuit, while in the latter the fall of potential is ascertained at any one setting by reading a voltmeter. We observe that in each instance a source of current is needed to produce the necessary potential difference to balance that of the gas chain, and a galvanometer is required for indicating when that balance has been established.

Within the past few years a number of instruments have appeared on the market, or have been described in the journals, which employ the potentiometer principle. Among them may be mentioned the "ionometer," of Bartell, which followed McClendon's description of a direct reading potentiometer; another instrument called an "ion-o-meter," described by Elliott; the Bovie potentiometer; the pyrovolter, employing the balanced potential principle; the Wendt titration outfit, employing Hildebrand's connections; the Kelley electrometric titration apparatus, designed for determinations of chromium vanadium and manganese in alloy steels, and utilizing the change in potential during an oxidation-reduction process; the Roberts outfit, used in determining minute quantities of ferrous in the presence of ferric oxides; the Eppley titration apparatus; Hendrixon's improvised potentiometer, for iodometric titrations; the Type K potentiometer, the portable H-ion potentiometer, and the automatic recording potentiometer of Leeds & Northrup Co.; and a number of others. With a list as formidable as this before him, the poor chemist, lacking guidance, must be quite at sea in the matter of making the proper selection for his particular problem.

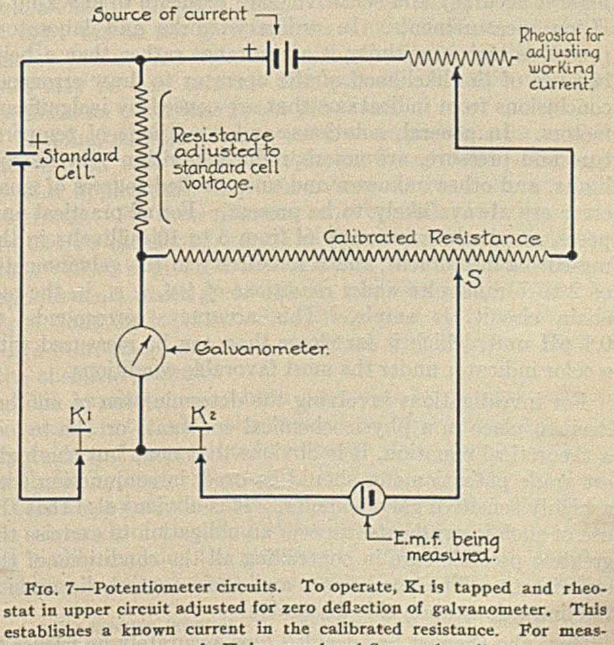

Fig. 7—Potentiometer circuits. To operate, K_1 is tapped and rheostat in upper circuit adjusted for zero deflection of galvanometer. This establishes a known current in the calibrated resistance. For measuring unknown e. m. f., K_2 is tapped and S moved until galvanometer shows zero. The position of S is then read on a scale which is calibrated directly in volts.

Selection of Apparatus

It is impossible, of course, to discuss each of these instruments, and state where it is applicable. The writer can give only a few general suggestions which will be helpful in determining what outfit best suits certain requirements.

IS THE HYDROGEN ELECTRODE APPLICABLE?—In the first place, we must know whether or not the hydrogen electrode will be well behaved in the solution under test. There are many complex solutions, containing substances that are likely to "poison" the electrode and cause it to disregard with great obstinacy the expectation that it will observe Nernst's law. The best course is either to borrow an outfit from someone, or to let someone who has an outfit test the solution in which you are interested. Some work has been done on "poisoning" of electrodes, and the writer has been informed that a method has been devised for restoring "poisoned" electrodes, and removing from them the tendency to misbehave at any future time. Some of the "poisons" that have been mentioned are formaldehyde, sulfides, ammonia, and certain nitrates. There may be other substances in the solution upon which the platinum black in the electrode exerts a catalytic action. In solutions containing charged colloidal particles, it is impossible to measure the H-ion concentration because of the presence of these particles. According to Bovie, the silver remaining in a solution after precipitation with hydrochloric acid is sufficient in quantity to "poison" the electrode completely.

It is well to have at hand a buffer solution of known pH value which is altogether free from suspicion of poisoning the electrode. An electrode which in the test solution behaves peculiarly can then be quickly tested in the buffer solution, to determine whether or not it is poisoned. Should it, in this solution, give an indicated voltage far different from the value it should give for the known pH, a new electrode should be used. Several tests, on different electrodes, should be made before the hydrogen electrode is rejected as a possibility.

WHAT IS THE DESIRED ACCURACY OF MEASUREMENT?—Assuming that the hydrogen electrode will work, we should decide as to the accuracy with which the measurements are to be made. The impression prevails that instruments of highest accuracy and sensitivity are requisite to any kind of H-ion measurements. In ordinary works and laboratory processes high sensitivity is a hindrance rather than a help, because of the likelihood of the operator to draw erroneous conclusions from indications that are caused by insignificant factors. In general, solutions, and conditions of temperature and pressure, are not reproducible within very narrow limits, and other unknown and uncontrolled sources of small error are always likely to be present. For all practical purposes, an absolute accuracy of from 5 to 10 millivolts in the measuring instrument, and a sensitivity in the galvanometer of 2 to 5 millivolts *under conditions of test, i. e.*, in the gas-chain circuit, is ample. This accuracy corresponds to 0.1 pH unit, which is far closer than can be measured with a color indicator under the most favorable conditions.

For investigations involving the determination of another decimal place in a physicochemical constant, or the test of a theoretical equation, it is obvious that none but the highest grade potentiometer should be used, in conjunction with a highly sensitive galvanometer. It is obvious also that the use of such instruments imposes an obligation to exercise the greatest possible care in controlling all the conditions of the experiment. The conditions, and their control, lie outside the limitations upon this discussion.

Once the chemist has decided how accurately he wishes to measure, his choice of apparatus among the different available kinds will be largely influenced by his own ideas as to suitability of design and convenience of manipulation of the apparatus under consideration, and, to a minor degree, upon the persuasive power of the salesman offering it.

The Calomel Electrode

There is little choice among the various available designs. Each has some merits. Simplicity in this as well as in other parts of the apparatus is much to be desired. As regards the selection of degree of saturation of potassium chloride solution, concentrations greater than 0.1 N are to be recommended. Mudge and Fales have shown that the saturated potassium chloride electrode is extremely stable, that it minimizes resistance of the gas chain, and that slight changes in saturation have very little effect upon its potential. The same statement holds for the N KCl solution to a lesser degree. The latter has an advantage over the former in that no troublesome "creeping" of solution and crystallization of salt outside the vessel occurs, although in the former case the trouble from creeping can be obviated by setting limits to it with vaseline or paraffin.

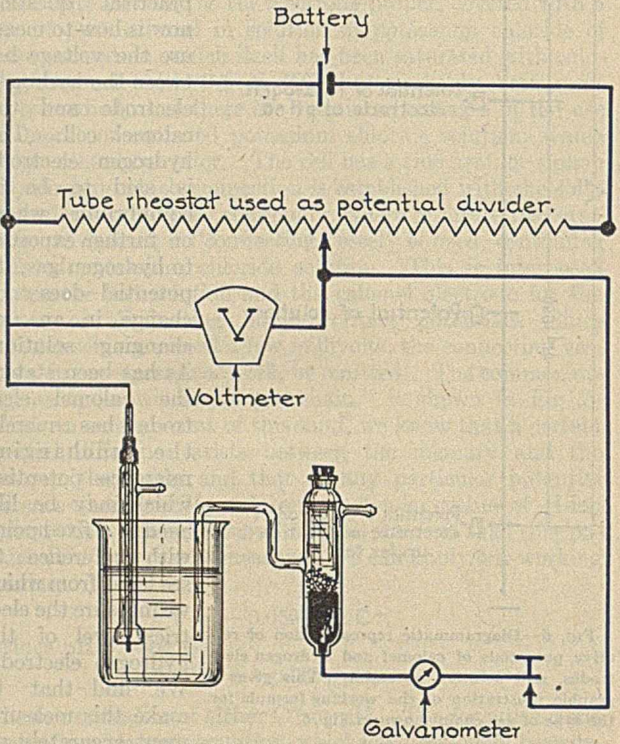

FIG. 8—Hildebrand's connections for measuring gas-chain voltage. The e. m. f. from the gas chain is balanced by adjustment of the potential divider until galvanometer shows zero. The voltmeter, permanently connected as shown, then reads the potential difference which was required to balance the unknown e. m. f.

The reservoir vessel should contain potassium chloride of the same concentration as that in the cell, saturated with calomel. The cell should be flushed out from time to time by allowing some of the stock solution to run through the siphon arm. This prevents contamination of the cell from the testing solution. In flushing, care should be taken to displace all air bubbles in the siphon tube, since these introduce a high resistance into the galvanometer circuit and render the indications sluggish and insensitive.

In work of the degree of accuracy we are considering, the connecting vessel may be omitted for reasons already stated. Errors due to liquid junction potentials are least when a calomel electrode with saturated potassium chloride is used.

THE HYDROGEN ELECTRODE

Successful deposition of platinum black on the electrode is a fairly simple matter, for which there are many methods. A procedure which the writer has found invariably successful is to use a weak solution of platinic chloride—about 2 per cent—and, after having most thoroughly cleaned the platinum, introduce the electrode and a piece of clean platinum wire, or another electrode, into the solution. These two electrodes are connected to two dry cells in series. As soon as there is a copious evolution of gas, reverse the connections, and continue reversing at the same indication, for several minutes. The intervals between reversals will be 10 to 15 seconds.

Some workers prefer to use gold as the base upon which to deposit the platinum black, while others have gold-plated their platinum base. Presumably this shortens the time for the electrode to reach equilibrium because of the smaller absorption of hydrogen by gold than by platinum.

The basis for choice of any one of the many forms of hydrogen electrode described in the literature cannot be gone into here. In general, the bubbling type (Hildebrand, Bovie, Wendt) is satisfactory for a great variety of measurements.[8]

SOURCE OF HYDROGEN

The most convenient source of hydrogen is the steel drum containing the compressed gas, readily obtainable in most cities. Electrolytic hydrogen is desirable. The drum should have a reducing valve for regulation of gas pressure, and the gas is led to the apparatus preferably through copper tubing or undercured gum tubing, to reduce loss of gas by diffusion. Electrolytic generators on a laboratory scale have been used with success, employing sodium hydroxide with nickel or iron electrodes. The Kipp generator is also a suitable source. In any case, the gas should be passed through wash bottles containing solutions for removal of such impurities as oxygen, arsine (from impure zinc in Kipp generator), acids, and possible traces of foreign gases which might previously have been in the hydrogen cylinder. A common practice is to pass the gas first through alkaline permanganate, then pyrogallol, and finally pure water. When small quantities of solutions are being titrated or tested, *e. g.*, in a culture tube or other small vessel, the gas itself serves admirably as an agitator. In larger vessels, a mechanical stirring device is necessary for intimate mixing during a titration.

TEST OF APPARATUS

One test has already been mentioned, to determine the condition of the hydrogen electrode. The same kind of test is excellent as an over-all check of the apparatus. This consists of using a standardized buffer solution of any convenient pH value in place of the test solution, and measuring the voltage. If this is only several (10 to 20) millivolts different from the calculated value for that particular pH, it is probable that the difference is a departure in the calomel electrode from the assigned value for the concentration of potassium chloride being used, and to other sources of minor e. m. f.'s. Adjustment can then be made in the calculations. A check on this test is to use another solution of different pH and to note whether the same difference in millivolts is observed.

It is to be noted that with a preliminary test of this sort it is unnecessary to devote much painstaking work to making up the calomel electrode. The only requirement is that its electrode potential be unvarying, and this condition becomes established within several days after preparation of the cell.

MEASUREMENT OF pH—When it is desired to know the actual H-ion concentration or pH of a given solution, a direct measurement of voltage of the gas chain is sufficient, from which the desired value is calculated.

CONVERSION OF MEASURED VOLTAGE INTO pH

This is accomplished by using the formula previously given: $\mathrm{pH} = \frac{V-v}{0.0591}$. V is the observed voltage, and v the calomel cell potential referred to the hydrogen electrode at pH=0; the factor 0.0591 is the number of volts corresponding to one pH interval at 25° C. There is a small temperature correction which in routine work at "room" temperature may be disregarded. The otherwise necessary computations are eliminated by the use of tables.[9] A still simpler and more convenient way is to use a specially designed slide rule of straight or circular pattern, as recently described by the writer.[10] An ordinary slide rule is also a great convenience, although in this case a mental subtraction ($V-v$) must first be made.

ELECTROMETRIC TITRATION

This application of the hydrogen electrode with its measuring and indicating instruments is one of the most important, from the chemist's standpoint. Titration with a standardized acid or basic solution to some particular end-point (equivalent point), and adjustment of a medium to a particular pH value for optimum experimental conditions, are illustrations.

The usual titration curves, of the type obtained by Hildebrand,[11] are obtained by plotting voltage or pH against volume of solution added. Near an equivalent point there is a sudden and usually large change in voltage. This change, shown by a sudden large galvanometer deflection, may be taken as an indication of the equivalent point, or where higher accuracy is needed, a curve may be plotted and the equivalent volume more closely estimated. An accuracy of one or two parts per thousand is easily obtained. When the pH of an equivalent point is known, or when it is desired to adjust a solution to a definite pH value, the voltage may be set for the proper value, and titration continued until the galvanometer shows a balance. In all such measurements a light tap on the galvanometer key should be employed until a balance has been nearly obtained, after which the circuit may be kept closed. This precaution avoids upsetting equilibrium conditions in the gas chain.

In a limited time it is impossible to do justice to an enumeration, even with the briefest descriptions, of the many successful applications that have been made of the hydrogen electrode. For these reference must be made to the literature. In Clark's excellent book "The Determination of Hydrogen Ions" there is given a bibliography, classified according to applications, which gives one an excellent idea of what has been done up to 1920. Since that time other applications have been made, and more are added with each new issue of the chemical journals.

One application has been suggested by several chemists interested in teaching, the value of which is borne out in the experience of those who have made electrometric titrations with the hydrogen electrode. It deserves special emphasis. There is probably no method or apparatus that can be put in the hands of a student which is so illuminating and which so readily explains the meaning of such terms as "acidity," "actual reaction," "total reaction," "alkalinity," "hydroly-

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[8] Other practical points in connection with the use of the hydrogen electrode are mentioned in Leach's "Food Inspection and Analysis," 4th edition, 1027.

[9] For example, Schmidt and Hoagland, *Univ. Calif. Pub. Physiol.*, **8** (1919), 23.

[10] *Science*, **54** (1921), 153.

[11] *J. Am. Chem. Soc.*, **35** (1913), 847.

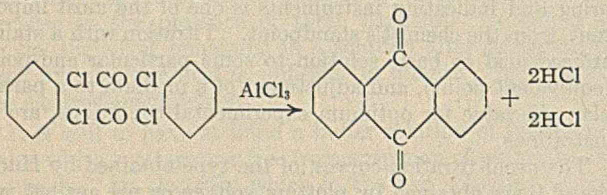
sis," and others, as a simple apparatus for measuring hydrogen electrode potentials. With a clear understanding of these matters he has a "stock in trade" which will save him much perplexity and which will aid him in clear insight into many of the problems which he must tackle when he begins the practice of his profession.

The Reactions of Phosgene with Benzene and *m*-Xylene in the Presence of Aluminium Chloride[1,2]

By Robert E. Wilson[3] and Everett W. Fuller

Research Laboratory of Applied Chemistry, Massachusetts Institute of Technology Cambridge, Massachusetts

On account of the great reduction in the cost of producing phosgene, which was brought about by war-time developments, this Laboratory has undertaken a study of possible new methods of utilizing this reactive compound in certain syntheses which now appear to be within the range of commercial possibility. The initial aim of the work described in this article was to produce anthraquinone from phosgene and benzene by the Friedel and Crafts reaction:



Although anthraquinone was not secured, the results obtained are of interest, as they represent a much more thorough study of the reactions between phosgene and benzene (and its homologs) than has been published previously.

The reaction between phosgene and benzene in the presence of anhydrous $AlCl_3$ *gives benzoyl chloride and benzophenone but no trace of anthraquinone.*

The reaction takes place in two stages, with the intermediate formation of the compound $C_6H_5COCl{:}AlCl_3$ *which can be hydrolyzed to give benzoic acid. This reacts very rapidly with more benzene, however, and the final product is almost entirely benzophenone irrespective of changes in temperature, method of mixing, ratio of reacting substances, etc.*

When CS_2 *is used as a diluent a large part of the product can be obtained as benzoic acid. Evidence is presented to show that this is due to the slight solubility of the intermediate benzoyl chloride-*$AlCl_3$ *compound in* CS_2 *which is thus removed before it has opportunity to react with more benzene.*

m-Xylene gives with phosgene a di-xylyl ketone with at least two of the methyl groups ortho to the carbonyl group.

Attempts to change this di-xylyl ketone to a derivative of anthraquinone by oxidation were not successful.

In one of their early papers, Friedel and Crafts[4] mention that by adding anhydrous aluminium chloride to a mixture of benzene and phosgene, they secured benzophenone and a small amount of benzoic acid. No trace of anthraquinone was found. Later experimenters[5] used xylene in place of benzene and obtained the corresponding phenones and acids, but no evidence of a quinone linkage was reported. No further work on the reactions of phosgene with benzene, toluene, or xylene is reported in the literature to the knowledge of the authors.

Attempts to Make Anthraquinone

By varying the experimental conditions the attempt was made to carry the reaction beyond the stage of the formation of benzophenone and thus secure anthraquinone. However, by none of the methods tried was it found possible to cause more than one phosgene molecule to react with a single benzene molecule even when a large excess of phosgene was used. For additional proof, benzophenone was treated with phosgene and aluminium chloride at different temperatures. There was no evidence of any reaction taking place and the benzophenone was recovered unchanged. Also, benzoyl chloride was treated with an equivalent amount of aluminium chloride in the hope that two molecules might mutually react with each other and thus give anthraquinone. But no reaction was noted up to near the boiling point of the benzoyl chloride, when charring and decomposition of the latter took place. No definite new compound could be isolated.

These results are in accord with the customary observation that it is very difficult to make two negative groups enter an aromatic ring ortho to each other. They also agree with the results of V. Meyer[6] who found it impossible to put two acetyl groups on benzene by the Friedel and Crafts reaction.

By reducing the benzophenone to diphenylmethane it was, however, found possible to make it react with more phosgene, but the resulting product was tarry, and was not identified. This indicates again that the negativity of the keto group is what prevented further reaction with the phosgene.

Reactions between Phosgene and Benzene

Although there seemed to be little likelihood of being able to prepare anthraquinone by this method, a study was made of the principle factors influencing the reaction between phosgene and benzene to form benzoyl chloride and benzophenone.

The mechanism of the action of aluminium chloride in the Friedel and Crafts reactions has been studied by a number of investigators.[7] For reactions of the above type, the chloride appears to form a compound with one or both of the reacting substances and thus to render them active. In the case of phosgene, three fairly stable molecular compounds with aluminium chloride are claimed to have been isolated,[8] while with benzoyl chloride and benzophenone molecular compounds, containing mole for mole, have been found. The aluminium chloride thus bound up renders its own molecule active but is not available for activating other molecules.

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[1] Presented in preliminary form before the Division of Organic Chemistry at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

[2] Published as Contribution No. 42 from the Research Laboratory of Applied Chemistry, M. I. T.

[3] Director, Research Laboratory of Applied Chemistry, M. I. T.

[4] Friedel, Crafts and Ador, *Ber.*, **10** (1877), 1854.

[5] Ador and Pelliet, *Ibid.*, **11** (1878), 399.

[6] *Ber.*, **29** (1896), 1413.

[7] Boeseken, *Rec. trav. chem.*, **19** (1900), 19; **20** (1901), 102; **24** (1905), 6; Perrier, *Ber.*, **33** (1900), 815; Krarberg, *J. prakt. chem.*, **61** (1900), 494.

[8] Band, *Compt. rend.*, **140** (1905), 1688.

TABLE I—REACTIONS BETWEEN BENZENE AND PHOSGENE
(All quantities are given in relative moles)

No.	Benzene	Phosgene	$AlCl_3$	CS_2	Benzoic Acid	Benzophenone	$\frac{\text{Benzoic Acid}}{\text{Benzophenone}}$	METHOD
1	4	Excess	1	..	0.01	0.89	..	Phosgene into benzene and $AlCl_3$ at 4° C.
2	4	Excess	1	..	0.01	0.87	..	Phosgene into benzene and $AlCl_3$ at 80° C.
3	4	2	1	..	0.01	0.55	..	Benzene to mixture of phosgene and $AlCl_3$
4	2	1	1	..	0.01	0.55	..	$AlCl_2$ to mixture of benzene and phosgene
5	2.5	1	1	..	0.01	0.63	..	$AlCl_3$ to mixture of benzene and phosgene
6	2	1	1	..	0.01	0.70	..	Same as 4 and kept under 1 atmos. gage pressure
7	2.5	1	1	..	0.01	0.75	..	Same as 4 and kept under 1 atmos. gage pressure
8	2	1	0.23	..	0.01	0.18	..	$AlCl_3$ to mixture of benzene and phosgene
9	2	1	0.35	..	0.01	0.27	..	$AlCl_3$ to mixture of benzene and phosgene
10	1	1	1	..	0.01	0.48	0.021	$AlCl_3$ to mixture of benzene and phosgene
11	1	1	1	0.10	0.05	0.43	0.116	$AlCl_3$ to mixture of benzene and phosgene
12	1	1	1	0.50	0.10	0.41	0.244	$AlCl_3$ to mixture of benzene and phosgene
13	1	1	1	1	0.25	0.33	0.760	$AlCl_3$ to mixture of benzene and phosgene
14	1	1	1	2	0.36	0.29	1.24	$AlCl_3$ to mixture of benzene and phosgene
15	1	1	1	2.5	0.33	0.23	1.43	$AlCl_3$ to mixture of benzene and phosgene
16	1	1	1	4	0.38	0.25	1.52	$AlCl_3$ to mixture of benzene and phosgene
17	1	1	1	4	0.59	0.17	3.47	Benzene added drop by drop to others—kept cold
18	1	1.5	1	4	0.01	0.39	..	$AlCl_3$ added very slowly to others
19	1	Excess	1	4	0.01	0.25	..	Phosgene added very slowly to others
20	2	1	1	4	0.03	0.52	..	$AlCl_3$ to mixture of benzene and phosgene
21	..	..	..	..	0.01	0.24	..	Al amalgam in benzene + HCl and then + phosgene
22	..	..	..	..	0.01	0.16	..	Al + $HgCl_2$ in benzene + phosgene
23	..	..	..	..	0.01	0.08	..	Al in benzene + HCl + phosgene
24	..	..	..	..	No action		..	Anhydrous $FeCl_3$(1 mole)

EXPERIMENTAL STUDY OF BENZENE-PHOSGENE REACTIONS

EXPERIMENTAL METHOD—In studying the effect of changing various conditions, the general method of procedure was as follows, unless otherwise specified. A weighed amount of phosgene was absorbed in a known amount of benzene cooled with ice and salt. The aluminium chloride was then added slowly and the flask was allowed to stand in the ice bath for several hours until the reaction had proceeded to a considerable extent and then was left at room temperature for 12 to 15 hrs. The mixture was then added to ice water, which decomposed the aluminium chloride compounds with the separation of an oil consisting of benzophenone, benzoyl chloride, and any excess benzene that might be present. The oil was treated with caustic soda solution to hydrolyze the benzoyl chloride and remove it as sodium benzoate. On acidification of the extract benzoic acid was precipitated and recovered. In the following work the benzoyl chloride is reported as benzoic acid. The remainder of the oil was dried and fractionally distilled to give benzene and benzophenone.

EFFECT OF DIFFERENT VARIABLES—The effect of various conditions of the yields and on the course of the reactions may be determined from a study of the data given in Fig. 1 and in Table I. In considering the yields relative values should be given greater weight, as small differences in actual yields were unavoidable even under the same experimental conditions. All yields were based upon the purified product.

Time—Fig. 1 indicates the results that were secured by removing 100-cc. samples at various times from a mixture of relative moles of phosgene and aluminium chloride in an excess of benzene that was maintained at 4° C., and analyzing for benzoyl chloride and benzophenone. The formation of excess benzoyl chloride, over that reacting with more benzene to give benzophenone, starts in slowly, gradually increases, and reaches a maximum in 5 to 6 hrs., after which it falls off again. Benzophenone also starts in very slowly but constantly increases to a maximum at somewhat less than 24 hrs. The reaction is evidently completed within 24 hrs., at 4° C.

A two-stage reaction with the intermediate formation of benzoyl chloride is clearly indicated. Thus it will be noted that at the very start of the reaction more benzoyl chloride than benzophenone is found. As time goes on the reaction as a whole accelerates, as measured by the total conversion of benzene to one of the two forms; but the quantity of intermediate product increases comparatively slowly while the end-product increases rapidly. The maximum rate of forming benzophenone coincides with the maximum momentary concentration of benzoyl chloride, as would be expected. Thereafter, as the rate of forming benzoyl chloride drops off, as a result of exhaustion of the *phosgene*, the small excess which had been built up quickly disappears, and eventually benzophenone is substantially the only product obtained.

It is not possible to make an exact comparison because of certain uncertain variables having to do with the formation of the aluminium chloride compounds, but it would appear from these data that the *specific* reaction rate between benzoyl chloride and benzene is about ten times as great as that between phosgene and benzene under conditions similar to those prevailing above. It is accordingly impossible, under such conditions, to carry the reaction on anywhere nearly to completion without having the end-product present in much larger amounts than the intermediate product (eventually benzoic acid).

Since the latter material is the only one with a large market at the present time, much of the following work had as its immediate aim the altering of the conditions of the reaction so as to favor the formation of benzoic acid rather than benzophenone, either by speeding up the first reaction or slowing down the second. The yields of the product per mole of the more expensive raw materials (aluminium chloride and phosgene) were also of importance.

Temperature—Expts. 1 and 2 in Table I were run in an identical way except for the temperature difference. The yields and products were the same.

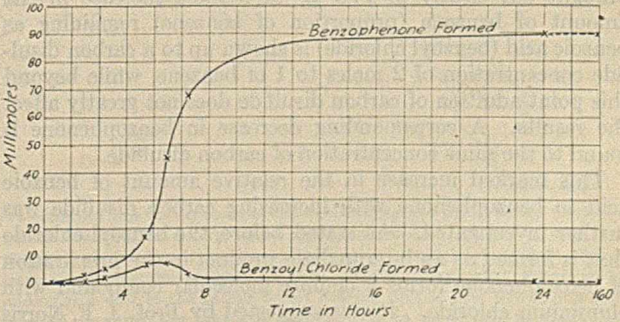

FIG. 1

Method of Mixing—As shown in Table I, Expts. 1, 2, 3, 4, etc., the methods of mixing the constituents were varied in all possible ways. The products were always the same, however, and the yields were not affected where the same proportions of constituents were used.

Pressure—The result of using pressure is indicated in Expts. 6 and 7. Pressure probably acts simply as a means of hindering escape of phosgene and thus gives a somewhat higher yield.

Proportion of Constituents—The molecular proportions of constituents are given by the equations for the reaction and must be used to secure anything approaching 100 per cent yields. On account of the volatility of phosgene an excess of it or of benzene helps the yields per mole of the other constituent by maintaining sufficient gas throughout the run to give the theoretical yields. The effect of increasing amounts of aluminium chloride is shown in Expts. 8, 9, and 4. One mole of aluminium chloride is evidently united with and removed from its active state by each mole of product formed and so a theoretical amount of aluminium chloride must be used. As stated before, these molecular compounds of aluminium chloride have been isolated, but in further confirmation of their formation in these reactions a crystal obtained in one of the experiments was analyzed and found to correspond to the formula $C_6H_5COC_6H_5.AlCl_3$.

Substitutes for $AlCl_3$—Several substitutes for aluminium chloride were tried, as is indicated in Expts. 21, 22, 23, and 24, but none of these proved satisfactory. Anhydrous ferric chloride can be used in place of aluminium chloride in many of the Friedel and Crafts reactions, but with phosgene and benzene it appeared to be inert.

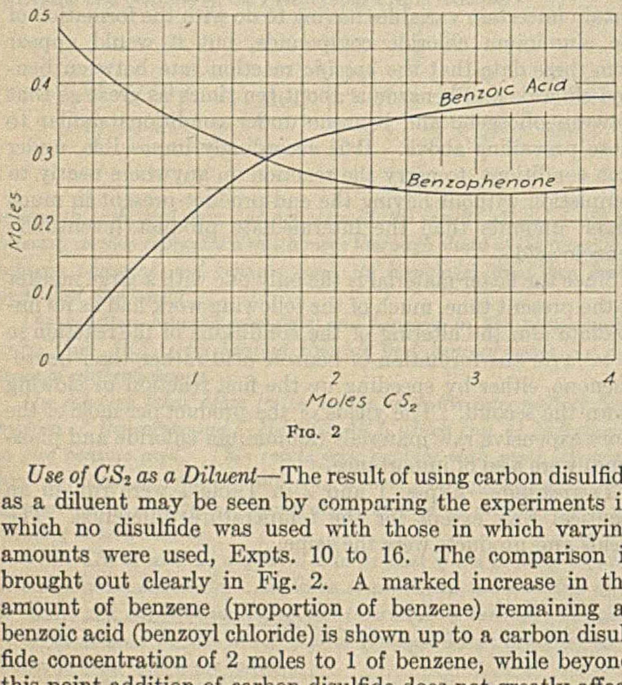

FIG. 2

Use of CS_2 as a Diluent—The result of using carbon disulfide as a diluent may be seen by comparing the experiments in which no disulfide was used with those in which varying amounts were used, Expts. 10 to 16. The comparison is brought out clearly in Fig. 2. A marked increase in the amount of benzene (proportion of benzene) remaining as benzoic acid (benzoyl chloride) is shown up to a carbon disulfide concentration of 2 moles to 1 of benzene, while beyond this point addition of carbon disulfide does not greatly affect the results. A corresponding decrease in benzophenone is found to the same concentration of carbon disulfide.

This marked increase in the relative amount of benzoic acid to benzophenone with increasing carbon disulfide was further investigated. As stated before, the benzoyl chloride that is formed as an intermediate product in the preparation of benzophenone forms a definite molecular compound with aluminium chloride. It was suggested by Prof. J. F. Norris that this intermediate molecular compound might be rendered less soluble in the reacting medium by the presence of CS_2. It would thus be removed from the sphere of activity with a resulting increase in the relative amount of benzoic acid obtained in hydrolysis.

Solubility data obtained in this Laboratory[9] indicate this explanation to be correct. The benzoyl chloride-aluminium chloride compound was isolated as a yellow solid and its solubility determined for varying mixtures of carbon disulfide and benzene. The results follow:

Per cent CS_2	Temperature 4° C. Per cent Benzene	Solubility G. per 100 Cc.
100	0	1.4
75	25	2.6
50	50	7.7

Furthermore it was noticed that in runs where carbon disulfide was used and the yields of benzoic acid were high a heavy dark oil separated out in the bottom of the flask. Although this substance was a liquid where a solid would be expected, it undoubtedly contained the benzoyl chloride-aluminium chloride compound which was thus separated to some extent from the incoming benzene. The composition of the dark oil was not constant, but an analysis of that obtained at the end of one of the runs gave 9 per cent of benzoic acid, 53 per cent aluminium chloride, 17 per cent of benzophenone, and 21 per cent of phosgene, with possibly a little benzene.

Further to prove this point, Expt. 17 was made, in which benzene was dropped very slowly into a cold mixture of carbon disulfide, phosgene, and aluminium chloride. This gave the best possible conditions for precipitating the intermediate molecular compound out of solution as it is formed and before it could come in contact with more benzene. As was expected, the yield of benzoic acid was very large and that of benzophenone was low, and some procedure similar to this is probably the best way to obtain a high yield of benzoic acid. On the other hand, when either aluminium chloride or phosgene was added very slowly to a mixture of the other three, it gave a chance for each new mole of benzoyl chloride to react with more benzene; thus the principal product was benzophenone, as shown in Expts. 22 and 23.

The above experiments with carbon disulfide were all made with just one mole of benzene for each mole of aluminium chloride and phosgene and the discussion holds only for such a case. If, however, more than a mole of benzene is used per mole of aluminium chloride, the product will eventually be all benzophenone, since the intermediate compound will slowly redissolve and react with the excess benzene if sufficient time is allowed. Expt. 20 indicates this. Where no carbon disulfide is used, on the other hand, the much greater solubility of the benzoyl chloride-aluminium chloride compound in benzene brings about complete reaction to benzophenone, regardless of the ratio between benzene and aluminium chloride used (Expts. 1 to 10).

COMMERCIAL POSSIBILITIES[10]—While the foregoing investigation has not been directed primarily to the commercial aspects of the process, it seems worth while to consider briefly this phase of the problem.

Although the listed price of benzophenone is quite high, it has little use except for scientific purposes and the demand is not large enough to warrant a commercial installation. If its availability at much lower prices should ever develop a demand for this product, the above-described method is certainly admirably adapted for commercial production, as the yields are high (85 to 90 per cent), the product clean, and the raw material cost quite low, a very small fraction of the present quotations for pure benzophenone.

For benzoic acid, on the other hand, there is a very ready market, and material such as that prepared by the above reaction, which is entirely free from chlorine in the ring (as distinguished from the product made by chlorinating toluene, which gives trouble in this respect), has a large and active market. It is for this reason that the effort was made in the foregoing study to increase the yield of benzoic acid as compared with benzophenone, and this was found possible by slowly adding benzene to the other components dissolved

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[9] D. I. Gross, undergraduate thesis, M. I. T.

[10] The recommended process has been covered by U. S. Patent Application.

in carbon disulfide. The cost of this process on a commercial scale depends partly on the losses of carbon disulfide and on whether the process can be made continuous by drawing off the lower layer of oil and adding the other constituents to the carbon disulfide. The small amount of benzophenone found as a by-product could be readily converted to benzoic acid by fusing it with caustic soda (recovering the benzene evolved), dissolving in water, and acidifying with sulfuric acid. This process gives 90 per cent yields without difficulty.

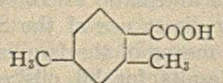
Another possible process would be to carry the reaction through to benzophenone without the use of any carbon disulfide, and then to form benzoic acid by the above-mentioned fusion process applied to the entire product. The high chemical cost of this process would be largely or entirely counterbalanced by the more rapid reaction rate and the absence of the fire risk and losses attendant upon the use of large amounts of carbon disulfide.

Rough estimates of the total costs of these two processes indicate that it should be possible to produce chlorine-free benzoic acid for about the present quotations (60 cents per lb.) for the present U. S. P. material, not allowing for sales cost or profits. If there should be enough demand for benzophenone to consume the small amount produced as a by-product in the carbon-disulfide process, or if the price of chlorine-free benzoic acid should be stabilized around 80 cents per lb., the process would appear to have distinct commercial possibilities.

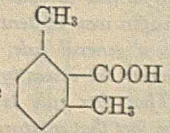
Reaction between Phosgene and Meta-Xylene

A brief study was made of the product formed by the reaction of phosgene and xylene in the presence of aluminium chloride. Phenyl-*o*-tolyl ketone is known to give anthraquinone on heating with lead oxide or with manganese dioxide and sulfuric acid.[11] It has also been shown that phosgene and xylene react to give a ketone with at least two of the methyl groups ortho to the carbonyl group.[12] The attempt, therefore, was made to bridge across these ortho methyl groups of di-*m*-xylyl ketone by oxidation and thus to secure a substituted anthraquinone.

PREPARATION OF DI-*m*-XYLYL KETONE—*m*-Xylene was prepared by the boiling of a commercial xylene (b. p. 138° – 142°) with dilute nitric acid (1:3) for several days to oxidize the *o*- and *p*-xylenes, and then washing with caustic soda solutions, steam distilling, and carefully fractionating with a column containing glass beads. A xylene was thus secured boiling at 139.0° to 139.4°, where *m*-xylene boils at 139.2°. This xylene was treated with phosgene and aluminium chloride and the resulting product was worked up in the usual way. The dixylyl ketone was secured in the form of an oil boiling at 345° to 348°. The reaction was similar to that for the formation of benzophenone, except that when carbon disulfide was used as a diluent the *m*-xylene gave only a very small amount of an acid derivative even when the reaction was carried out under the conditions that had proved most favorable for the formation of benzoic acid. The acid formed in the case of *m*-xylene was entirely



melting at 126°.

CONSTITUTION OF DI-*m*-XYLYL KETONE—Since it was necessary to have one or more of the methyl groups in the dixylyl ketone ortho to the carbonyl group in order to be able to oxidize the ketone to an anthraquinone derivative, the positions of these methyl groups were first checked up.[13] The ketone was fused with caustic soda and the acids secured from the resulting sodium salts were determined. The major portion consisted of the  acid melting at 126° and which gave an amide melting at 179°. About 10 per cent was the  acid melting at 97° to 99°. Each of these acids indicates a carbonyl group in the ketone with at least two methyl groups ortho to it.

OXIDATION OF DI-*m*-XYLYL KETONES—Attempts to oxidize the dixylyl ketone were made at various temperatures. Lead oxide, manganese dioxide and sulfuric acid, potassium dichromate in acid and alkaline solutions, potassium permanganate in acid and alkaline solutions, and fusion with sodium peroxide had no effect upon the ketone. Potassium dichromate in concentrated sulfuric acid and chromic oxide in acetic acid decomposed the ketone while nitric acid in sulfuric acid formed nitro derivatives. Refluxing with 1:1 nitric acid gave a semisolid mass from which a calcium salt of an acid was separated. This yielded 9.4 per cent CaO on ignition, which corresponds to one mole of calcium to two moles of dixylyl ketone acid (9.7 per cent CaO). The oxidation, therefore, resulted merely in attacking one of the methyl groups in each molecule. No further attempts at oxidation were made.[14]

Acknowledgment

The writers desire to express their appreciation of the many helpful suggestions of Dr. C. S. Venable and Dr. J. F. Norris.

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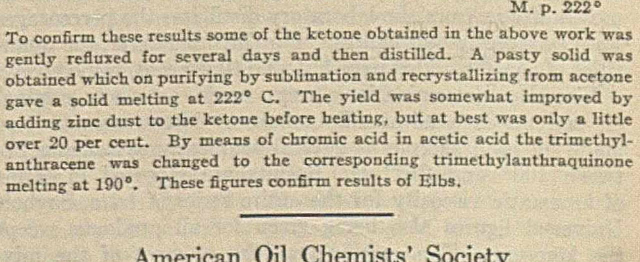
[11] Behr and van Dorp, *Ber.*, **6** (1873), 754; **7** (1874), 16.

[12] Ador and Meier, *Ibid.*, **12** (1879), 1968; Elbs, *J. prakt. chem.*, [2] **35** (1887), 481.

[13] Ador and Meier and Elbs in their work on dixylyl ketones did not definitely determine the positions of the methyl groups in the ketone, but appear to have assumed the structure from the reactions of the ketone and from the fact that they recovered some 1-carboxyl-2,4-dimethylbenzoic acid, during the preparation of their dixylyl ketone.

[14] Elbs (*Loc. cit.*) shows that the xylyl ketone on long heating loses a molecule of water and goes to trimethylanthracene, which on oxidation gives a trimethylanthraquinone.



M. p. 222°

To confirm these results some of the ketone obtained in the above work was gently refluxed for several days and then distilled. A pasty solid was obtained which on purifying by sublimation and recrystallizing from acetone gave a solid melting at 222° C. The yield was somewhat improved by adding zinc dust to the ketone before heating, but at best was only a little over 20 per cent. By means of chromic acid in acetic acid the trimethylanthracene was changed to the corresponding trimethylanthraquinone melting at 190°. These figures confirm results of Elbs.

American Oil Chemists' Society

The 13th Annual Meeting of the American Oil Chemists' Society will be held at the Grunewald Hotel, New Orleans, La., May 8 and 9, 1922. An unusually interesting program is being arranged and a large attendance is expected.

Notwithstanding business conditions, the American Oil Chemists' Society has made notable progress this year not only in its membership but in its extended activities.

Effect of Paraffin Wax on Viscosity of Petroleum Oils[1,2]

By E. W. Dean[3] and M. B. Cooke[4]

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Experiments have been performed to determine the effect upon viscosity of changing the paraffin wax content of several petroleum oils. It was found that, as a general rule, the viscosity of any mixture is intermediate between the viscosity of the paraffin and that of the wax-free oil. That this rule is approximate rather than absolute is proved by the fact that mixtures of paraffin and an oil of practically equal viscosity were slightly less viscous than either of the constituents.

Paraffin wax, when dissolved in oil, behaves like an oil of low viscosity at temperatures considerably below its melting point.

Commercial paraffin wax is a complex mixture which can be easily resolved into fractions of differing physical properties.

A need for information on the relation between paraffin wax content and viscosity of petroleum oils was recently encountered. The lack of published figures and unsatisfactory character of the information supplied to the Bureau by individuals associated with the petroleum refining industry led to the belief that this subject had probably never been given the detailed study which it merits and therefore experiments, the results of which are recounted herein, were undertaken.

Acknowledgment is made of the assistance rendered in experimental determinations by L. E. Jackson, formerly petroleum chemist, and F. W. Lane, organic chemist, of the Pittsburgh petroleum laboratory of the Bureau. A preliminary report[5] covered the results of Mr. Jackson's work.

SCOPE OF INVESTIGATION

The work involved measurements of the viscosities of several commercial petroleum oils before and after adding predetermined percentages of commercial paraffin, and similar tests upon two distillates specially prepared in the laboratory from crude oil, before and after removing successive portions of crystalline wax. The commercial oils used were water-white kerosene, transformer oil, spindle oil, medium automobile oil, and Liberty aero oil. All the oils and the wax used were, according to the best available information, derived from Pennsylvania crude petroleum. The laboratory distillates were also derived from Pennsylvania crude oil and were very similar in general character to crude "wax distillates" as prepared in oil refineries. The paraffin wax was a well-known brand, sold largely for household use.

Changes in wax content varied from a fraction of 1 per cent up to 10 per cent. For experiments involving the removal of wax from the laboratory distillates the percentages were necessarily odd figures. For the other tests, the quantities of paraffin added were 1, 5, and 10 per cent, respectively.

Viscosity determinations were made on each original oil and on each oil-paraffin mixture. Measurements were made on each sample at several temperatures ranging between 100° and 210° F. Results are reported in terms of kinematic viscosity for the entire series of tests, Saybolt Universal figures also being given for all products except the kerosene. The specific gravities of most of the mixtures are also reported, which makes it possible to calculate absolute viscosities if such figures are desired.

To obtain supplementary information, the several products studied were subjected to conventional physical tests. Experiments were also performed to demonstrate that commercial paraffin wax is a mixture of constituents which vary appreciably in physical properties.

EXPERIMENTAL

DESCRIPTION OF PRODUCTS STUDIED—The two laboratory distillates were prepared by distilling a 5-gal. charge of Pennsylvania crude petroleum in an electrically heated iron still equipped with a coil for supplying "open" steam. The primary fractions obtained by means of this "steam" distillation were redistilled in a vacuum of 40 mm., and final products obtained that came over between temperature limits of 250° to 275° C. (482° to 527° F.), and 275° to 300° C. (527° to 572° F.).

TABLE I—PHYSICAL PROPERTIES OF PRODUCTS USED IN EXPERIMENTS

NATURE OF PRODUCT	Specific Gravity at 60° F.	° Bé.	Flash Point[1] ° F.	Fire Point[1] ° F.	Saybolt Universal Viscosity at 100° F.	Saybolt Universal Viscosity at 130° F.	Saybolt Universal Viscosity at 210° F.
Water-white kerosene	0.795	46.1	...	...	....	....	....
Laboratory distillate[2]	0.835	....	...	...	53.8	43.4	34.3
Laboratory distillate[3]	0.847	....	...	...	69.2	50.8	36.3
Transformer oil	0.852	34.3	340	395	72.7	51.7	36.5
Spindle oil	0.883	28.6	415	480	212.7	111.0	46.8
Medium auto oil	0.883	28.6	420	470	283.0	141.0	52.0
Liberty aero oil	0.888	27.7	475	530	874.0	383.0	89.1
Paraffin wax[4]	.....	....	...	...	....	52.0	37.0

[1] Cleveland open cup.

[2] Distillation limits at 40 mm. vacuum, 250° to 275° C. (482° to 527° F.).

[3] Distillation limits at 40 mm. vacuum, 275° to 300° C. (527° to 572° F.).

[4] Melting point of paraffin wax, 126.0° F.; specific gravity at 130° F., 0.7830.

The commercial products were obtained from refining companies operating and marketing in the Pittsburgh district. The physical properties of both the laboratory and commercial products are indicated by figures in Table I.

OPERATING DETAILS—The method of separating wax from the laboratory distillates was an adaptation of the commercial process of "filter pressing" wax distillate. The actual procedure involved forcing the cooled oil through a specially designed pressure filter, the separating medium being ordinary filter paper. The quantities separated were determined by weighing the wax scraped from the filter paper after the liquid oil had been driven through. The resultant figures are, of course, only approximate, but the accuracy is sufficient for present purposes.

Additions of wax to the commercial oils were made on the basis of percentage by weight of paraffin in the mixture. Viscosity determinations were made either with the Saybolt Universal viscosimeter or with Ostwald viscosimeters. The latter instruments were calibrated so that results could be expressed in terms of either kinematic viscosity or Saybolt viscosity. The kinematic viscosity equivalents of the figures obtained by direct use of the Saybolt viscosimeter were calculated by means of the familiar Bureau of Standards equation.[6] Results for all oils except the kerosene are reported in terms of both systems of viscosity units.

DISCUSSION OF RESULTS

Results of the principal series of viscosity tests are shown in Table II.

It will be observed that the viscosity of the original oil has a marked influence on the effect of changes in wax con-

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[1] Received January 11, 1922.

[2] Published by permission of the Director, U. S. Bureau of Mines.

[3] Petroleum Chemist, Pittsburgh Experiment Station, Bureau of Mines.

[4] Assistant Petroleum Chemist, Pittsburgh Experiment Station, Bureau of Mines.

[5] E. W. Dean and L. E. Jackson, "The Effect of Crystalline Paraffin Wax upon the Viscosity of Lubricating Oil," *Bur. Mines, Repts. of Investigations* **2249**, May 1921.

[6] $\text{Kinematic viscosity} = 0.00220 \times \text{Saybolt viscosity} - \frac{1.80}{\text{Saybolt viscosity}}$.

Table II—Changes in Viscosity Caused by Varying Paraffin Wax Content of Several Petroleum Oils

Description of Oil	Percentage Change Paraffin Content of Oil	Specific Gravity at 100° F.	Saybolt Universal Viscosity at			Kinematic Viscosity at		
			100° F.	130° F.	210° F.	100° F.	130° F.	210° F.
Water-white kerosene	0	0.7800	....	....	....	0.01930	0.01415	0.00842
	+ 1	0.7805	....	....	....	0.01864	0.01446	0.00857
	+ 5	0.7810	....	....	....	0.01994	0.01532	0.00902
	+ 10	0.7812	....	....	....	0.02166	0.01655	0.00958
250° to 275° C. laboratory distillate[1]	0	....	53.8	43.4	34.3	0.0849	0.0539	0.0230
	− .5	....	(51.4)	43.5	34.3	(0.0781)	0.0543	0.0230
	−1.9	....	54.5	43.7	34.4	0.0870	0.0548	0.0234
	−2.5	....	54.7	43.8	34.3	0.0874	0.0551	0.0230
	−3.3	....	54.9	43.9	34.2	0.0880	0.0555	0.0228
275° to 300° C. laboratory distillate[1]	0	....	69.2	50.8	36.3	0.1262	0.0763	0.0303
	−1.5	....	(64.5)	50.7	36.1	(0.1139)	0.0760	0.0295
	−3.0	....	69.1	50.7	35.9	0.1260	0.0760	0.0290
	−5.9	....	68.7	50.3	35.9	0.1250	0.0749	0.0290
	−9.0	....	71.4	51.0	36.3	0.1320	0.0769	0.0303
Transformer oil	0	0.8400	69.3	51.7	36.5	0.1264	0.0789	0.0310
	+ 1	0.8391	68.3	51.5	35.9	0.1239	0.0783	0.0288
	+ 5	0.8374	67.3	51.2	35.1	0.1213	0.0775	0.0260
	+ 10	0.8353	67.5	50.8	34.5	0.1218	0.0760	0.0237
Spindle oil	0	0.8691	213	111	46.8	0.4602	0.2280	0.0642
	+ 1	0.8683	206	109	45.0	0.4445	0.2233	0.0590
	+ 5	0.8656	188	100	43.3	0.4040	0.2020	0.0537
	+ 10	0.8606	168	91.5	43.0	0.3589	0.1816	0.0527
Medium automobile oil	0	0.8703	283	141	52.0	0.6162	0.2974	0.0798
	+ 1	0.8675	257	137	50.9	0.5584	0.2883	0.0766
	+ 5	0.8581	246	128	50.4	0.5339	0.2675	0.0752
	+ 10	0.8615	215	115	48.2	0.4646	0.2374	0.0687
Liberty aero oil	0	0.8744	874	384	89.1	1.923	0.8448	0.1758
	+ 1	0.8723	826	359	87.8	1.817	0.7898	0.1727
	+ 5	0.8698	688	319	78.3	1.514	0.6962	0.1492
	+ 10	0.8650	561	272	72.5	1.234	0.5918	0.1341

[1] Some viscosity measurements for the two laboratory distillates were made at temperatures slightly different from those listed. The figures given are interpolated to permit tabulation on an equivalent basis.

tent. Addition of wax to the kerosene increased its viscosity. The change in the case of the two laboratory distillates is practically negligible. For the other four oils there is a decrease in viscosity, as a result of adding paraffin, the decrease varying with the viscosity of the original oil. For example, the maximum decrease for the transformer oil is of the order of 5 per cent and for the Liberty aero oil is of the order of 35 per cent.

The obvious conclusion is that this investigation is simply one phase of the familiar general problem of the viscosity of mixtures. The effect of the paraffin wax seems to be practically identical with what might have been expected if, instead of the wax, a liquid oil of equal viscosity had been used. Actual measurements (see Table I) showed that at temperatures above its melting point, the viscosity of the paraffin was approximately the same as that of the transformer oil. When mixed with the more fluid kerosene it caused an increase in viscosity, and when mixed with the more viscous oils there was a decrease.

The transformer oil and the two laboratory distillates might seem to be exceptions to the simple qualitative rule that holds for the other products. The wax and transformer oil are practically equal in viscosity, and the mixtures are less viscous than either of the constituents. This occurrence, though interesting, is not at all surprising, as the viscosities of oil blends are usually less than the values calculated by the most satisfactory rule for additivity.[7]

There is a more definite explanation for the results obtained with the two laboratory distillates. Neither of these products showed appreciable changes in viscosity when various percentages of paraffin were removed. These two oils were considerably different in viscosity, and as a logical inference it was to be expected that the properties of the paraffin removed from one distillate would not be identical with those of the paraffin removed from the other. The separated paraffin, unfortunately, was not retained, and this probability could not be investigated by direct experimentation.

It was shown, however, that the wax used in the other tests could be resolved without difficulty into fractions of differing physical properties. To determine this experimentally a 15-g. sample of paraffin was dissolved in 7.5 g. of pure benzene by warming to a temperature of approximately 60° C. The solution was then cooled to 30° C., and the resulting crystals of wax were removed by filtration. The benzene was then removed from both "precipitate" and "filtrate" by evaporating for 3 hrs. on a steam bath. The yield of paraffin from the precipitate was approximately 7 g., while that from the filtrate was 8 g. The properties of the original paraffin and of the two fractions are indicated by the figures in Table III.

Table III—Showing That Commercial Paraffin Wax Is a Mixture of Constituents Having Varying Physical Properties

Nature of Material	Melting Point ° F.	Saybolt Universal Viscosity at 150° F.
Commercial paraffin	126	44
Fraction separating at 30° C. from a solution of 2 parts by weight of paraffin in 1 part by weight of benzene	132	46
Fraction remaining in solution at 30° C. when 2 parts of paraffin were dissolved in 1 part of benzene	119	42.5

It will be noted that even so simple a method of separation as this shows that commercial paraffin wax is a mixture of constituents of differing physical properties. Such being the case, it is entirely justifiable to assume that the paraffin separated from the laboratory fraction distilling between the limits of 250° to 275° C. is less viscous than that separated from the 275° to 300° C. fraction.

It has been impossible to formulate a quantitative rule for the effect of varying the paraffin wax content of oil from the figures in Table II. In a majority of cases the decreases or increases in viscosity are of such size as to be somewhat influenced by normal experimental errors in the determinations; furthermore, there is no satisfactory general rule for calculating the viscosity of blends. The method outlined by Herschel[7] is admittedly only an approximation, and is particularly unsatisfactory for mixtures in which the relative percentages of constituents are so different.

One of the most interesting facts brought out by these experiments is that, when dissolved in oil, paraffin wax seems to behave like an oil of low viscosity at temperatures appreciably below its melting point. Its effect upon viscosity at 100° F., which is 26° F. below its melting point, is similar to its effect at 130° and 210° F. The temperatures at which the oil-wax mixtures would begin to deviate from the general—though perhaps indeterminate—rules covering the viscosity of blends were not determined, but it seems safe to assume that they are related to the so-called cloud points, or points at which solid paraffin begins to separate.

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[7] W. H. Herschel, "Saybolt Viscosity of Blends," *Bur. Standards, Technologic Paper* **164** (1920).

Notes on the Chemistry of Lime Liquors Used in the Tannery[1]

By W. R. Atkin

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The following paper describes an extension of the theories of Procter and Wilson and of Loeb to the alkaline swelling of hide in lime liquors. The real reason why such "sharpening" agents as sodium sulfide and sodium carbonate produce greater swelling is that the osmotic pressure of sodium collagenate is greater than that of calcium collagenate at the same hydrogen-ion concentration. The smooth grain of skins unhaired by arsenic sulfide is due to the fact that only calcium collagenate is produced. A rapid method for the analytical control of lime liquors by swelling experiments on hide powder is described. Alkaline swelling is shown to be exactly analogous to acid swelling, which has been much more extensively investigated, and certain tanning processes are shown to act in a parallel way to acid pickling.

THE process of liming consists of soaking softened hides or skins in alkaline liquors, generally containing lime, for the purpose of rendering the hair loose so that it may be scraped off by means of an unhairing knife or machine. The unhairing action is generally supposed to be due to solution of the *rete malpighi* by the action of alkalies, sulfides and enzymes secreted by bacteria which are able to function even in such strongly alkaline liquors. Simultaneously with this action there occurs a swelling or plumping of the fibers which has a pronounced effect upon the nature of the final leather. The object of this paper is to present an explanation of the different swelling effects produced by varying the procedure of liming.

Stiasny[2] differentiates between plumping and swelling, but as the degree of plumping is not an easily measurable quantity, our work was confined to measurements of swelling. Plumping will be studied later.

In practice lime liquors are generally "sharpened" to increase the rate of unhairing by the addition of such substances as sodium sulfide, arsenic sulfide, and sodium carbonate. The sodium salts increase the alkalinity of the liquors through the formation of sodium hydroxide and there is an increased plumping of the skins. Stiasny has shown that the conditions favorable to rapid unhairing are obtained when the proportion of sodium hydroxide to sulfhydrate is unity. Sodium sulfhydrate exerts a strong solvent action on the keratinous matter. When red arsenic sulfide is used, it is slaked with the lime and the resulting solution is found to unhair quickly, but without increased plumping or swelling of the skins. Stiasny has shown that the unhairing action is due to the formation of calcium sulfhydrate and that the arsenic plays no important part, merely being converted into calcium sulfarsenite. Chrome tanners use this mixture because it causes goat skins for glacé kid to have a smoother and silkier grain when finished.

THEORETICAL CONSIDERATIONS

In order to obtain a good working knowledge of the theory of the swelling of hides and skins in alkaline solutions, it is necessary to understand the work of Procter,[3] Procter and Wilson,[4] and Loeb,[5] who have studied the action of acids, alkalies, and salts upon gelatin. The swelling of gelatin in acids or alkalies is due to the formation of an ionizing salt, such as gelatin chloride, and as the gelatin ion is nondiffusible, the acid-treated gelatin may be likened to an osmometer—the outer solution passing into the jelly until equilibrium is attained. Gelatin is an amphoteric substance; its isoelectric point is at $\mathrm{pH} = 4.7$, corresponding to a hydrogen-ion concentration of $10^{-4.7}\ N$. At any higher pH the gelatin is an equilibrium mixture of isoelectric gelatin and metal gelatinate, whereas at any pH lower than 4.7 there is a mixture of isoelectric gelatin and gelatin-acid salt.

Since collagen is very closely related to gelatin it would be expected to behave like gelatin, just as do other proteins such as egg albumin and casein. This has been found to be the case, and experiments at Leeds have shown the isoelectric point of collagen (or hide powder, which is the nearest approach to pure collagen we have) to be at a pH of about 4.8, which is almost identical with that of gelatin.

Loeb has shown that such properties as swelling, osmotic pressure, and viscosity depend on the hydrogen-ion concentration in the swollen protein. As the outer solution of acid or alkali is in equilibrium with the protein, these properties therefore depend also on the hydrogen-ion concentration of the outer solution, provided we are dealing with solutions of acids or alkalies alone. The addition of salts introduces further complications. The writer[6] has shown by calculations based on the theory of protein swelling put forward by Procter and Wilson that the results of these workers agree remarkably well with the results of Loeb and of Miss D. Jordan-Lloyd,[7] although the methods of experiment differed greatly in character. The results obtained by the above workers show that at $\mathrm{pH} = 2.4$ for the outer solution of acid in equilibrium with gelatin (corresponding to $\mathrm{pH} = 3.0$ in the jelly) a maximum swelling is attained with such acids as hydrochloric, nitric, phosphoric, tartaric, citric, acetic, and formic—this maximum being practically the same for all the different acids. Sulfuric acid also shows a maximum at the same pH value, but in this case the swelling is only about half that in the case of the other acids mentioned. Loeb explains this fact as follows: Hydrochloric, nitric, and phosphoric acids, etc., behave as monobasic acids forming salts of the type Gel-Cl, Gel-NO_3, but sulfuric acid acts as a dibasic acid, forming $(\mathrm{Gel})_2SO_4$. If we have equivalent quantities of the chloride and the sulfate at the same pH, the swelling is proportional to the osmotic pressure and that of the gelatin ion is negligible; hence the osmotic pressures are proportional to Cl^- and $^1/_2\,SO_4^{--}$. It is clear that the chloride swells more than the sulfate, roughly in the ratio of 2:1.

Similarly, sodium, potassium or ammonium gelatinate would swell more at corresponding pH values than would the salts of calcium or barium.

EXPERIMENTS ON HIDE POWDER

In order to test whether such reasoning could be applied to collagen the following experiments were carried out:

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[1] Presented before the Division of Leather Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] *Gerber*, **1906**; *J. Soc. Leather Trades' Chem.*, **3** (1919), 129.

[3] *Kolloidchem. Beihefte*, **2** (1911), 243; *J. Am. Leather Chem. Assoc.*, **6** (1911), 270; *J. Chem. Soc.*, **105** (1914), 313.

[4] *J. Chem. Soc.*, **109** (1916), 307.

[5] *J. Gen. Physiol.*, **1918–1920**.

[6] *J. Soc. Leather Trades' Chem.*, **4** (1920), 248, 268.

[7] *Biochem. J.*, **14** (1920), 147.

Half-gram lots of Standard hide powder were weighed out into 100-cc. graduated flasks, which were then filled up to the mark with different concentrations of solutions of sodium, barium[8] or calcium hydroxide which had been prepared with CO_2-free distilled water. The flasks were corked and left for 24 hrs. in an incubator at 25°. The corks were then replaced by pieces of rubber tubing closed by a spring clip in the middle. The other end of a rubber tube was connected to a buret sealed at the bottom and containing sufficient mercury to come up as far as the scale divisions. After the inverted flask was connected to the buret, the spring clip was slipped off and the swollen hide powder was allowed to settle down into the buret. The flask was shaken occasionally in order to collect all the hide powder in the buret and after 3 hrs. the volume of powder was read off from the buret. The equilibrium alkaline solution was filtered and an aliquot portion titrated. By means of tables the pH values were calculated, allowing for the different degrees of dissociation of the different alkalies. The volume of the swollen hide powder corresponded to the swelling.

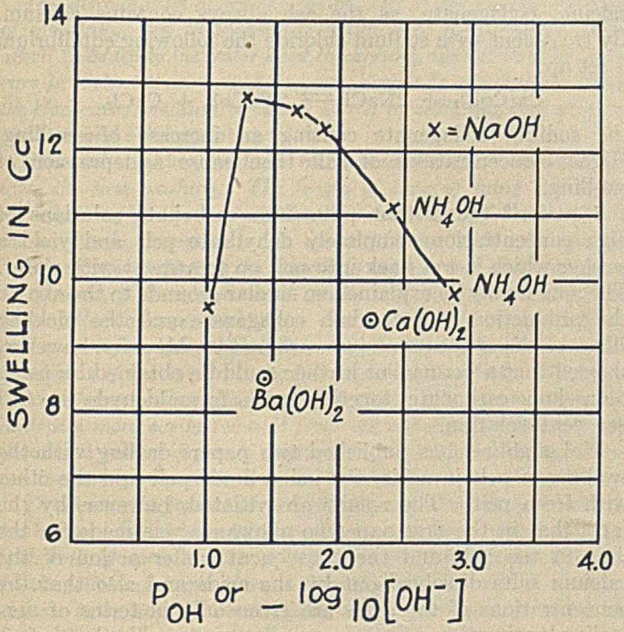

FIG. 1

Similar experiments were carried out with sodium hydroxide and calcium hydroxide, in solutions which were also made 0.05 M in $BaCl_2$ and 0.1 N in NaCl.

The results of the experiments are given in Tables I and II.

TABLE I

Normality of Equilibrium Solution		Equivalent to pH Value of	Swelling of Hide Powder, Cc.
$Ba(OH)_2$	0.0405	12.55	8.5
$Ba(OH)_2$	0.016	12.11	7.9
$Ba(OH)_2$	0.007	11.81	9.7
$Ba(OH)_2$	0.0025	11.38	9.7
$Ca(OH)_2$	0.006	11.75	9.4
NaOH	0.113	12.99	9.6
NaOH	0.055	12.70	12.8
NaOH	0.022	12.31	12.6
NaOH	0.014	12.12	12.3
NH_4OH	0.865	11.60	11.1
NH_4OH	0.0935	11.11	9.8
Distilled water		6.4	5.85

The addition of salt to the alkali-swollen collagen effects a repression of swelling exactly as in the case of pickling, when salt produces a remarkable falling effect on acid-swollen skins. Doubtless, the repression would be greater with more concentrated salt solutions, but it is distinctly perceptible with 0.1 N NaCl.

TABLE II

Final pH	Swelling Cc.	Final pH	Swelling Cc
$Ba(OH)_2$ plus $BaCl_2$ (0.1 N)		$Ba(OH)_2$ plus NaCl (0.1 N)	
12.55	6.9	12.56	10.1
12.13	7.5	11.81	11.0
11.84	8.4	11.46	10.8
11.46	8.7		
NaOH plus NaCl (0.1 N)		NaOH plus $BaCl_2$ (0.1 N)	
12.68	10.8	12.65	8.1
12.27	11.6	12.29	8.8
11.98	12.3	11.83	10.2

The results recorded in Table II are easily explained by the Procter-Wilson theory and show that alkaline swelling is governed by the same laws as acid swelling.

The results obtained upon adding sodium chloride to the barium hydroxide solutions and barium chloride to the sodium hydroxide are also given in Table II. Although neutral salt has a tendency to repress swelling, we find here that the mixture of sodium chloride with barium hydroxide produces more swelling than does barium hydroxide alone and also that barium chloride produces a bigger depression than an equivalent amount of sodium chloride, if added to collagen swollen with caustic soda. These results confirm for collagen the conclusions arrived at by Loeb for the action of alkalies on gelatin. In the experiments mentioned above we are really dealing with a reversible reaction of the type

$$Ba^{++}\ (Coll)_2^- + 2Na^+\ Cl^- \rightleftharpoons 2\ Na^+\ Coll^- + Ba^{++}\ Cl_2^-,$$

the relative proportions of the four constituents being governed by the law of mass action.

The addition of sodium chloride to barium collagenate tends to form sodium collagenate which has a bigger swelling capacity. Where barium chloride is added to collagen swollen with sodium hydroxide (sodium collagenate) the barium collagenate formed has a lower swelling power and the swelling is further depressed by the neutral salt present.

APPLICATION OF THEORY TO TANNING PRACTICE

This extension of the Procter-Wilson-Loeb theory to the alkaline swelling of hides provides explanations for several phenomena that have been described by various workers and also for some practical and empirical methods used by tanners.

ARSENIC SULFIDE—Probably the most important of these is the use of arsenic sulfide already mentioned. Despite the high cost of this substance it is preferred by chrome tanners for liming skins for glacé kid because of the smooth grain obtained. It is obvious that if a skin is excessively swollen during the preliminary stages of leather manufacture the grain will tend to become rough and coarse. Stiasny has shown that the use of arsenic sulfide is dependent on the production of calcium hydrosulfide, together with calcium sulfarsenite. The consequence is that only a calcium collagenate swelling takes place, and this is repressed to some extent by the soluble calcium sulfarsenite produced.

SODIUM SULFIDE—If, however, the cheaper sodium sulfide were used sodium hydroxide and hydrosulfide would be produced and the swelling would then be partly due to sodium collagenate and therefore greater. This effect would be further increased by the addition of more hydroxide ions arising from the hydrolysis of the sodium sulfide and consequent precipitation of some calcium hydroxide to keep the solubility product of the latter constant. Thus the addition of sodium sulfide to lime gives rise to a distinct increase of swelling compared with lime alone and still greater than that produced by lime and arsenic sulfide. This increase of swelling would explain the coarser grain obtained by the use

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[8] Barium hydroxide has been used on account of its greater solubility, but a reference to Table I will show that calcium hydroxide gives practically identical results. Any conclusions arrived at for barium hydroxide or barium chloride will apply to calcium hydroxide or calcium chloride.

of sodium sulfide. Procter's suggestion that the addition of calcium chloride would permit the use of sodium sulfide for unhairing skins even for this delicate work is thus seen to have a sound theoretical basis. Guisiana has suggested a similar procedure. It will be noticed by reference to Table I that an increase of alkalinity from 0.05 *N* (which is approximately the strength of saturated lime water) to 0.1 *N* (or a rise of pH from 12.70 to 13.0) does not produce any increase in swelling but rather the reverse. In practice, however, if a lime liquor be strengthened with sodium sulfide or sodium carbonate, the hides or skins will be found to be much more plumped or swollen. This increased swelling was formerly thought to be due to the increased alkalinity, but it would seem more in accordance with the true facts of the case to ascribe it to the increased swelling due to sodium collagenate. Here, again, some calcium hydroxide would be forced out of solution by the increased alkalinity. The present writer and his collaborators[8] have proposed two methods for the determination of the caustic alkalinity of lime liquors, but in view of these results the simplest control of lime-yard liquors would be to carry out swelling experiments on hide powder exactly as described in this paper. The swellings could be plotted against pH values and in this way successive liquors could be checked and a graphical record preserved.

WASHING OF HIDES—It has been the custom of many sole leather tanners to wash out practically all the salt in the hides before they are limed. Reference to Table II will show that the presence of sodium chloride causes more swelling of barium collagenate than when barium hydroxide alone is used. The same effect will be shown with calcium collagenate. The sole leather tanner can use as a sharpening agent to promote swelling and plumping, the salt that is already present in the hides and need not wash it out before liming. This method of working has been used with success in a large sole leather yard in England.

The reason why such care has been taken by tanners to remove salt from the hide appears to be the fear that salt may be carried forward to the tan pits and produce a flat empty leather. The employment of the three-pit system of liming and subsequent deliming would remove practically all the salt before the hides went forward to the tan liquors.

AMMONIUM HYDROXIDE—An interesting confirmation of the results given in this paper was described by Stiasny. Calf skin with the hair on was soaked in 200 cc. of liquor consisting of 0.5 *N* ammonium hydroxide to which equivalent quantities of various chlorides had been added: 0.84 g. NaCl, 0.8 g. $CaCl_2$, or 1.76 g. $BaCl_2$ (Table III).

TABLE III—WEIGHT ABSORPTION (PER CENT) WITH VARIOUS CHLORIDES

	NH_4OH	$NH_4OH + NaCl$	$NH_4OH + CaCl_2$	$NH_4OH + BaCl_2$
After 1 day	58.6	37.4	15.5	14.1
After 2 days	65.5	45.8	14.9	19.8

The pickling effect of the salts was apparent in each case but the repression of swelling was much greater with barium and calcium chlorides. In the case of ammonia and ammonia plus sodium chloride the hair was quite loose after 4 days, but not in the cases where calcium or barium chloride was used. Stiasny suggested that the explanation might be due to the formation of complex ammonia compounds of the type $Ca(NH_3)_8Cl_2$, but it has been shown by J. Atkin and the writer[9] that the hydroxyl-ion concentration of ammonia solutions is not altered by the addition of sodium chloride or calcium chloride. The explanation of the differences in swelling is of course exactly the same as for the results given in Table II, but the differences in unhairing capacity seem to require further investigation.

EFFECT OF CONCENTRATION OF SALTS

The influence of salt solutions of various concentrations on gelatin has been investigated by H. R. Procter, who found that increasing concentrations of salt caused an increased swelling; this, however, attained a maximum and afterwards fell on increasing the concentration of the salt solution.

Commercial gelatin appears to be almost always on the alkaline side of the isoelectric point and really contains some calcium collagenate, as the ash always contains calcium. By treatment with sodium chloride the following equilibrium is set up:

$$Ca(Coll)_2 + 2NaCl \rightleftharpoons 2NaColl + CaCl_2,$$

the sodium collagenate causing an increase of swelling. Higher concentrations of salt then cause a depression of swelling.

Meunier[10] found that potassium carbonate solutions of high concentration completely dehydrate pelt and yield a leather which is wet back into pelt on treatment with water. The action may be explained on similar grounds to the above: the production of potassium collagenate and the pickling effect of the excess potassium carbonate. Meunier, however, showed that a permanent leather could be obtained by using potassium carbonate together with formaldehyde in 0.3 per cent solution.

McLaughlin[11] has published two papers dealing with the swelling of pelt in acids, one using limed pelt and the other with fresh pelt. The results are vitiated, however, by the facts that in the first paper no allowance was made for the lime in the pelt and the consequent buffer action of the calcium salts dissolved out by the acids and also that the concentrations of the acids are given only in terms of normality by titration and the normality so stated is that before equilibrium has been set up. It is well known that hide, like gelatin, takes up a certain amount of acid and therefore the concentration of the residual acid *after equilibrium* should be determined. Further, Loeb's work has shown that comparisons of swelling are only valid if made at the same hydrogen-ion concentration, but McLaughlin makes no determinations of this; furthermore, it is not possible to calculate it from the dissociation constants of the acids for the reasons given above. It is very much to be regretted that so much painstaking work has been to a large extent nullified by these omissions.

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[8] *J. Soc. Leather Trades' Chem.*, **4** (1920), 111, 236, 248, 268.

[9] *Ibid.*, **4** (1920), 236.

[10] *Collegium*, **1912**, 11, 54, 420.

[11] *J. Am. Leather Chem. Assoc.*, **15** (1920), 228; **16** (1921), 295.

The International Chemical Conference

The general program of the Third International Chemical Conference, to be held at Lyons, France, June 27 to July 2, inclusive, includes meetings of the Council, reports of committees and visits to factories in the vicinity. On July 2, the delegates will go down the Rhône by boat to the neighborhood of Marseilles, where they will have an opportunity to attend the second congress of industrial chemistry, which has been arranged by the Société de Chimie Industrielle.

This congress will be held July 2 to 7. Among the general questions which will be considered are the animal, vegetable, and mineral resources of the French colonies. In addition to this, fats, soaps, etc., will be discussed.

Professor Moody Succeeds Professor Baskerville

On March 27, Prof. Herbert R. Moody, for seventeen years connected with the Department of Chemistry of the College of the City of New York as Professor of Industrial Chemistry and Chemical Engineering, was unanimously appointed to the Directorship of the Department to fill the vacancy caused by the death of Prof. Charles Baskerville.

Lye Hominy: Its Discoloration and a New Process for Its Manufacture[1]

By Edward F. Kohman

Research Laboratory, National Canners' Association, Washington, D. C.

The discoloration of canned lye hominy is apparently the result of alkalinity, due to incomplete washing of the hominy. When alkali is added to the water used in canning, typical blackening occurs in a short time. Acid, however, cannot be added to counteract the blackening, because it causes starch to settle out, and produces too hard and solid grains.

Repeated washing produces no appreciable effect on alkalinity after the first washing. The length of time of lying does affect the alkalinity of the product, the pH value varying from about 6.50 for a 10-min. lying period to about 9.00 for a 50-min. period.

Other factors affecting the alkalinity are size and shape of grain. In general, a thin, flat, small grain will yield a more alkaline hominy than a large, thick grain. Treatment of the corn with hot or cold water before lying slightly decreases the alkalinity of the product, but drying of the corn in vacuo has no noticeable effect. The age of the corn has a marked effect on its behavior in hominy making. The hulls are more easily removed from old corn, and it consequently acquires a greater degree of alkalinity. On the other hand, the tips are less easily removed.

To prevent the formation of black discoloration, the pH value of lye hominy should be reduced as low as possible by ample washing with boiling water or even at higher temperatures under pressure. In the following paper there is described a scrubbing or abrasion process to be applied directly after lying, by means of which the outer layer of the grain may be removed. This treatment materially lowers the alkalinity; aids in removing the tips and bran layer, thus making possible a shorter lying process with a consequent lowering of pH and removes the outer layer, which was colored by the lying process, giving a hominy of pleasing white appearance. All other attempts to lower the pH value resulted in a less complete removal of tips and bran layer.

In the study of discoloration that occurs in canned corn, a tendency was observed for the corn showing the greatest discoloration to have a lower acidity, as determined by titration. It was thought, therefore, that the black discoloration of hominy might be due to some of the lye not being washed out. The resulting alkalinity would render the sulfur-bearing proteins less stable and favor the formation of hydrogen sulfide, and would also favor the precipitation of the low concentration of ferrous sulfide which is the black discoloring agent.

Accordingly, in March 1920, a pack of hominy was put up under commercial conditions with water containing, respectively, 10, 15, and 20 cc. 0.1 *N* sodium hydroxide per 100 cc., and also 10, 15, and 20 cc. 0.1 *N* hydrochloric acid per 100 cc., respectively. Within a few days a few grains against the junction of the body and end of the can containing even the smallest amount of alkali showed the black discoloration but the control remained normal. This gradually became more pronounced so that within a year the liquor became dark and a number of grains were black almost throughout. The pH value of the control hominy was 7.12; that of the hominy containing 10 cc. 0.1 *N* alkali per 100 cc. liquor was 8.06.

As the control did not develop any black even after more than a year, the effect of the addition of acid in preventing it, if any, could not be demonstrated. But another very marked effect of the acid should be noted. The starch seemed to settle to the bottom and formed a solid cake during processing which extended nearly half way up in the can. Moreover, the loose grains above it were of a rather firm and solid texture as compared with normal hominy. This phenomenon was observed in similar experiments carried out later, thus demonstrating the impossibility of using acid to counteract black formation.

In December 1920, a second pack was put up in another plant, in which 1, 2, and 4 cc. 0.5 *N* sodium hydroxide, respectively, were added per 100 cc. of water used for canning. Typical black began to form within a short time and gradually increased, while the controls were still free from black. For comparison with data given below, it should be stated that the pH of those packs were as given in Table I. All values for H-ion concentration recorded in this paper were determined on the hominy liquor by the electrolytic method.

TABLE I—EFFECT OF ALKALI ON BLACK FORMATION

Cc. 0.5 *N* NaOH added per 100 cc. H_2O	0	1	2	4
pH value	7.0	7.39	7.76	8.58
Black formation	−	+	+	+

EFFECT OF WASHING ON pH VALUE

To duplicate commercial conditions a pack was put up at the same time in which the amount of washing that the hominy received was varied. After lying, the hominy was run once through a Sprague brushing machine and then through a squirrel cage while cold water was being sprayed on to it. Then it was given nine 15-min. washings in the usual hominy tubs. In one experiment the washing was done with cold water. In the other, the water was brought to boiling each time. This required about half of the 15 min., so that in each washing the corn was treated for only about 8 min. with actually boiling water. Samples taken after each washing were canned. Contrary to expectations, the successive washings produced no appreciable effect on the alkalinity even from the first washing. The pH is given in Table II.

TABLE II—EFFECT OF WASHING ON pH VALUE

SAMPLE NO.	1	2	3	4	5	6	7	8	9
Cold washed	7.12	7.08	6.96	6.94	6.96	6.88	7.02	6.88	6.93
Hot washed	7.01	6.94	6.84	6.87	6.91	6.84	6.94	7.04	6.78

Two similar experiments with the same corn at the same plant gave the results closely duplicating the above.

So low a pH in commercial hominy is unusual. A sample of hominy from the same plant but of a previous year had a pH of 7.88. Only one other brand has come to the writer's attention in which the pH was below 7.0, whereas the average pH for commercial hominy is 7.5 or above. This was new-crop corn and the moisture content was still so high that the shelled corn did not "flow" smoothly but tended to "bank." It was thought that in this condition the hulls might be removed by a materially less severe lying process, with a consequently lower pH. The effect of the age of the corn will be discussed below.

To get a clearer insight into the effect of the washing process in making lye hominy, the following laboratory experiment was made. A 2100-g. sample of corn was lyed by boiling for 25 min. in 7 l. of lye solution containing 52.5 g. of sodium hydroxide. This is the equivalent of 1 lb. 85 per

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[1] Received November 9, 1921.

cent lye per bu. The hominy was dumped on a sieve and the lye solution rinsed off with a stream of cold water. Next 160-g. samples were weighed into 14 No. 2 cans. Half were filled with boiling distilled water and half with boiling tap water and all boiled in a calcium chloride bath. After 15 min. 6 cans of each lot were drained and again refilled with boiling distilled and tap water, respectively. After the next 15-min. period only 5 of each lot were so drained and refilled, etc., until there was only one can of each lot for the sixth draining. In this way all cans were cooked the same length of time but varied in the amount of washing they received. All were closed, cooked for 1.5 hrs. at 212° F., and finally for 70 min. at 240° F. (116° C.). Table III gives the results obtained upon examination of the cans the next day.

Table III

Times Drained	Wt. Ash of 25 Cc. Filtered Liquor Distilled Water Grams	Wt. Ash of 25 Cc. Filtered Liquor Tap Water Grams	0.1 *N* Acid Required to Neutralize Ash (Methyl Orange In-Indicator) Distilled Water Cc.	0.1 *N* Acid Required to Neutralize Ash (Methyl Orange In-Indicator) Tap Water Cc.	pH Value Distilled Water	pH Value Tap Water
0	0.0434	0.0432	4.40	3.95	7.84	7.82
1	0.0348	0.0338	3.15	2.80	7.57	7.56
2	0.0272	0.0285	2.35	1.95	7.44	7.61
3	0.0242	0.0248	1.90	1.60	7.38	7.28
4	0.0218	0.0217	1.70	1.35	7.38	7.54
5	0.0189	0.0223	1.40	1.30	7.37	7.50
6	0.0177	0.0200	1.30	0.90	7.43	7.48

It is apparent that after the first draining there is no consistent drop in the pH. There is, however, a gradual decrease in the weight and alkalinity of the ash of the liquor with each succeeding washing. Two plausible explanations may be offered in this connection. First, hominy presents a buffer mixture and as the alkali is washed out, the buffer is also washed out. This amounts to the same thing as dilution of a buffer solution which does not have its pH changed thereby. Second, the protein or other difficultly soluble material in the grain may have its pH altered during the lying process; such products would be washed out extremely slowly and yet might be soluble enough to affect the reaction of the liquor.

Effect of Intensity of Lying Process

In view of the above results, it was necessary to find elsewhere the cause for the great variation in pH observed in different brands of commercial hominy. One very important factor causing such variation in the reaction of hominy is the length of the lying period. The following experiment will illustrate. The corn was lyed in the usual way, and samples of equal weight were removed from the lying bath after 10, 20, 30, 40, and 50 min. Each sample was rinsed three times with about three times its weight of cold water. Each sample was then divided into three equal portions: the first was given one 15-min. cook, drained, then canned, and given a 150-min. cook at 212° F.; the second was given two 15-min. cooks, drained after each, then canned, and given a 135-min. cook; the third was given three 15-min. cooks, drained after each, then canned, and given a 120-min. cook. All were then processed at 240° F. for 70 min. in No. 2 cans. Thus all samples were cooked 165 min. at 212° F., and 70 min. at 240° F. after lying.

Table IV shows the effect of the different lying periods and the effect of subsequent washing or boiling out with water on the pH and on the titratable acidity and the alkalinity of the soluble ash.

The pH varies from about 6.50 for the 10-min. lying period to about 9.00 for the 50-min. lying period. Washing with boiling water has no appreciable effect on the pH, but it does decrease the titratable acidity of the liquor and the alkalinity of the soluble ash.

A similar experiment was made on a scale large enough to give a dozen cans of hominy for each lying period, with the idea of holding these cans to note the effect of the higher pH due to longer lying on black discoloration. The lowest pH of this experiment was 7.2 and the highest 8.2. No appreciable black had formed in four weeks, but after six weeks the hominy with the higher pH showed a number of discolored grains in the bottom of the can.

Table IV

Lying Period Min.	Times Boiled Out and Drained	0.1 *N* Alkali or Acid Required to Neutralize 100 Cc. Liquor (Phenolphthalein Indicator) Cc. Alkali	Cc. 0.1 *N* Acid Required to Neutralize Soluble Ash from 100 Cc. Liquor (Methyl Orange as Indicator)	pH Value
10	1	3.70	7.60	6.55
10	2	3.50	6.80	6.51
10	3	2.00	6.00	6.56
20	1	2.00	7.60	7.16
20	2	2.00	6.40	7.19
20	3	1.60	5.80	7.03
30	1	0.80	7.40	7.85
30	2	1.00	6.00	7.84
30	3	1.00	5.00	7.69
40	1	0.00	9.40	8.66
40	2	0.40	6.20	8.53
40	3	0.60	5.40	8.38
		Cc. Acid		
50	1	0.30	9.60	9.02
50	2	0.20	7.20	9.05
50	3	0.10	4.80	9.05

Size and Shape of Grain

There are a number of other factors which more or less influence the alkalinity of hominy. The size of the grain has an appreciable effect. From one lot of corn 200 g. of large grains and 200 g. of small grains were picked. Both were lyed alike and treated alike in other ways throughout the process. The hominy from the large grains had a pH of 7.66, whereas that from the small grains had a pH of 7.98. In general, a thin, flat, small grain will yield a more alkaline hominy than a large, thick grain.

Moisture Content of Corn

If the corn is treated with hot or cold water previous to lying (for example, with boiling water for 5 min. or cold water for 1 hr.) the alkalinity of the hominy is slightly less than when the corn is not so treated. The corn absorbs some water during this process which would tend to dilute the lye solution. But the above statement holds true even if the lye solution used for the unsoaked corn is diluted with an amount of water equivalent to that absorbed by the soaked corn. But the hulls are distinctly less removed in the case of soaked corn. Therefore, a longer lying period or more concentrated lye would be necessary to remove the hulls completely, and this would render the corn more alkaline. Apparently the water absorbed during the soaking period forms a protection against the penetration of the lye. Presumably the hot water forms a gelatinous coat of starch paste which acts in this manner.

Corn has been dried *in vacuo* at a low temperature before lying. In one case it lost 1.75 per cent moisture and in another case 3 per cent. In neither case was there any appreciable effect on the pH value of the hominy.

Age of Corn

In Table V are given the results obtained with old and new corn in January 1922. The new corn was from the 1921 crop and was raised from the seed selected from the crib from which the old corn was taken. The old corn was from the 1920 crop. In each case, 200 g. were lyed in 400 cc. of lye solution containing 5 g. of sodium hydroxide.

A very distinct difference in the behavior of the new and old corn is not brought out in Table V. On lying the old corn, the solution becomes much thicker or more viscous. This is also true of the wash water during the precook. The hull or bran layer is removed from the old corn by a shorter lying process, although the reverse is true of the tips, as is seen from the table. The old corn becomes darker in color, the germs become detached from the grains, which then tend to break. In Expt. I, when the lying period was 26 and 29 min., no count of the tips could be made for the old corn because so many grains were broken. This corn was distinctly overlyed. The old corn seemed to give a bigger swell, but there were so many inconsistencies in the different experiments that no definite figure can be given. All these differences between old and new corn are greatly diminished when the scrubbing process is used. This process overcomes the effect of overlying, and with it the old corn yielded a good hominy when lyed 26 or 29 min.

Table V—Effect of Age of Corn

	Expt. I Hominy not "Scrubbed"				Expt. II Hominy "Scrubbed"			
	pH Value		Per cent of Grains Still Having Tips on		pH Value		Per cent of Grains Still Having Tips on	
Minutes Lyed	New Corn	Old Corn	New Corn	Old Corn	New Corn	Old Corn	New Corn	Old Corn
20	7.41	7.98	31	47	7.20	7.55	18	28
23	7.60	8.40	24	36	7.26	7.84	9	18
26	8.00	8.69	..	..	7.51	7.95	8	13
29	8.08	8.55	..	..	7.73	8.07	7	8

Effect of Alkalinity, Hydrogen Sulfide, and Iron

A separate lot of hominy was made from each of a number of ears of good seed stock corn, selected from a large crib. The procedure was uniform for each. After the lying process each lot was rinsed with uniform amounts of cold water and dumped on a sieve where it was rubbed with the hand to remove more completely the surface softened by the lying process. The effect of such a procedure on the pH will be discussed later, but at the time this effect was not realized and a variable was thus introduced in the making of these separate lots. The hominy was again uniformly rinsed and given four 20-min. cooks in boiling water. One hundred grams of each lot were canned in No. 1 flat cans. Also 25 g. were put up in each of two glass test tubes about 1 in. in diameter, by sealing off the open end. Into each of the tubes for each ear was also introduced a strip of tin plate about $^5/_8$ in. wide and long enough to extend about $^3/_8$ in. above the liquor. This strip of metal was cut from a large piece of tin plate and thus the raw cut edges were exposed to the hominy. At the same time the iron was determined on the dry corn, the pH value of the resulting hominy, and also the hydrogen sulfide evolved upon heating the hominy at 120° C. for 45 min., at that stage of its preparation when it was ready to be canned. The method for this determination is to be described in a separate paper. The samples thus used were afterward canned in No. 1 flat cans, and are discussed below.

The corn put up in the glass tubes has been observed frequently and the extent of black discoloration recorded. In the tubes where this occurred there were in nearly all cases some signs of discolored grains within a very few days after packing. These samples of hominy were all put up between April 28, 1921, and May 20, 1921. The results up to the present time may be summarized as follows: Among those samples having the highest pH, more are discolored and the discoloration is decidedly worse than among those with the lower pH. The discoloration is in the order of the amount of hydrogen sulfide formed. The discoloration is also in the order of the iron content but the relation in this respect is not so marked. These results are in harmony with the fact that alkali, and to a less extent iron salts, hastens the breaking down of sulfur-bearing proteins, with the development of hydrogen sulfide.

It is apparent from an examination of these tubes of hominy that the iron to unite with the hydrogen sulfide must come from the tin plate. In every case its development began where the grains were in contact with the cut edge of the strip of plate. In no case was any sign of black formation found in the tubes containing no tin plate. This is also borne out by the data of Table VI, which gives the iron content of the germ and endosperm, based on dry weight, of commercially canned hominy. These figures are many times greater than the iron content of normal corn.

Table VI

Sample No.		1	2	3	4	5	6	7	8	9	10	11
Mg. Fe per kilo on dry basis	Endosperm	185	39	119	18	13	17	14	64	212	62	75
	Germ	5970	441	5460	501	368	1515	902	503	6670	1605	3160

Effect of Temperature of Precook

In the cans containing the hominy which had been used for the hydrogen sulfide determination (*i. e.*, which had had an additional 45-min. precook at 120° C. with live steam passed through it) the tin plate was decidedly brighter than in the cans containing the hominy treated only in the ordinary way. Such a procedure would be expected to lessen the tendency to black discoloration, in that it removes some of the hydrogen sulfide and is an efficient washing. A precook at 120° C. gave a much better swell and a better appearing hominy than the 100° C. precook. It enabled one to obtain more uniform fills, inasmuch as the swell was fairly complete before canning. A uniform fill is an important consideration from the standpoint of black formation. If the can is so full as to pack the hominy firmly against the walls, the hominy is more prone to discoloration than when loosely packed. Storing cans on the side is beneficial because the weight of the hominy does not pack the lower grains so firmly against the can.

It should not be inferred that a high precook would make unnecessary the usual number of washings with hot water. These are important in the prevention of black, even though they have no marked effect on the H-ion concentration. This is evident from Table I, where it is seen that there is abundant black formation when there is only enough sodium hydroxide present to produce a pH of 7.39.

Effect of Scrubbing

In seeking for ways to keep the pH as low as possible during the process of lying, it was observed that nearly every modification in the method was accompanied by a less thorough removal of the tips and bran layer. Any tips will of course detract from the appearance. This is also true of the incompletely removed bran layer, which gives the grains a "curly" or "fuzzy" coat. Moreover, a complete removal of the bran layer permits the grain to swell better.

A process has finally been developed which will decidedly lower the alkalinity of lye hominy and which should be entirely practicable and easy to apply on a commercial scale. This can be done by a process of scrubbing or abrasion by means of a drum made of No. 12 grater bodies, 9 in. long by 6 in. wide. Twenty of these bodies were soldered together in such a fashion as to form a cylinder 1 ft. long and 7.5 ft. in circumference. Ends for this cylinder were made of tin plate. A narrow sliding door was made to introduce the hominy. This drum was revolved at the rate of 45 r. p. m., in a pan of water of such depth that the hominy slid smoothly down as the drum turned instead of being carried up and dropped down.

A number of brushes were introduced inside this drum, but they only complicated matters and did no apparent good in the apparatus. It is possible that passing the hominy over such a grating surface while it was being shaken would prove more satisfactory. Possibly to some plants a continuous process would be best adapted. In such a case the effect of the length of the lying period must be duly taken into account. When a kettle of hominy is sufficiently lyed it is very essential that its entire contents be emptied at once and the hot lye solution thoroughly rinsed off. A scrubbing process in boiling water may be more effective and is worthy of being tried commercially.

It was found that in this size of drum a 5-min. rotation was about the optimum when 10 lbs. of corn were used. A 12-ft. cylinder would handle 120 lbs. in 5 min. or 600 lbs. in 25 min. The latter figures represent a normal factory batch and an average lying period. Therefore, there should be no practical difficulty in its use from this standpoint.

TABLE VII—EFFECTS OF SCRUBBING PROCESS

No.	43.5 Per cent NaOH Grams	Time of Lying Min.	Time of Scrubbing Min.	pH
1	1050	17	0	7.76
2	1050	17	5	7.26
3	1050	17	10	7.25
4	1050	17	15	7.26
5	1050	24	0	7.84
6	1050	24	5	7.42
7	1050	24	10	7.32
8	1050	24	15	7.22
9	1050	31	0	7.78
10	1050	31	5	7.46
11	1050	31	0	7.38
12	1050	31	15	7.26
13	1600	10	0	7.26
14	1600	10	5	6.92
15	1600	10	10	6.92
16	1600	10	15	6.91
17	1600	15	0	7.75
18	1600	15	5	7.34
19	1600	15	10	7.29
20	1600	15	15	7.23
21	1600	20	0	7.89
22	1600	20	5	7.39
23	1600	20	10	7.37
24	1600	20	15	7.38
25	750	18	0	7.22
26	750	18	5	7.02
27	750	18	10	6.94
28	750	18	15	7.06
29	750	25	0	7.28
30	750	25	5	7.17
31	750	25	10	7.04
32	750	25	15	6.98
33	750	32	0	7.74
34	750	32	5	7.50
35	750	32	10	7.34
36	750	32	15	7.24

There are three very decided advantages in such a procedure. First, it aids in removing the hulls or outer layer of the grains, in which is located the relatively highly alkaline product resulting from the lying process. Second, the usual lying process can be shortened because the mechanical abrasion in part takes the place of the lying process in removing the hulls. In this way it helps further to reduce the alkalinity. Third, by removing this outer hull so effectively it gives a whiter product than can be obtained by any other known process, except by bleaching, and the whiteness is not the dead chalky whiteness obtained by a bleaching process. It is the natural and pleasing whiteness of the corn which is lost in the present methods of hominy making.

Just how efficient a process of scrubbing will be in the prevention of discoloration in hominy cannot be stated without further observations. It will not be effective in all cases, for black has been observed when this process was used. The intensity of the lying process, *i. e.*, the time of lying and strength of the solution, plays a part. When the hominy acquires a high pH due to a severe lye treatment, it can be greatly reduced by abrasion of the grains, but it seems impossible to get it below a certain point, as Table VII will illustrate. It should not be inferred that the H-ion concentration is the only factor which determines the degree of discoloration. The beneficial effect of washing should not be underemphasized. This washing removes to a more or less extent the electrolytes which may have a solvent effect on the iron. Table I gives an example of a hominy with a pH value below the average for commercial hominy, yet the black formation occurred early and was marked. But there was more alkali in it than would be left in a well-washed hominy. In the commercial washing of hominy, the necessity of good stirring should be realized. Since the washing is done in boiling water, a certain amount of hydrogen sulfide is liberated, and less will be formed in the can during processing.

Thirty-six lots of twenty-four No. 2 cans each have been put up in the laboratory from the same corn. In these the time of lying, the strength of the lying solution, and the length of the scrubbing period were all varied to demonstrate the effect on the pH value. Forty pounds of corn were lyed for the time indicated in Table VII, in 80 lbs. of lye solution of the strength noted. It was then rinsed thoroughly, divided into four equal parts, one used as control and the others scrubbed for 5, 10, and 15 min., respectively. Each was then given four 20-min. cooks, and then canned in No. 2 cans, 230 g. per can. The pH was determined a month or more after canning. It should be stated that Nos. 13 to 16, inclusive, and 25 to 36 were all underlyed, not all the tips being removed, even after scrubbing. Half of the cans are stored on end and half on the side. See Table VII.

APPEARANCE AND LOCATION OF BLACK DISCOLORATION

These packs have scarcely been up long enough to justify final conclusions, but it has been noticed that when a can of hominy is allowed to stand on end undisturbed, after processing, there are two ways in which the black ferrous sulfide may show up.

1—A variable amount always forms on the inner surface of the top of the can, notably on the expansion rings and possibly more adjacent to the end seam. So much may form as to flake off, giving the hominy a peppered appearance. It is very similar in appearance to the black which forms in the air space in canned peas and sweet corn. It was evident from these experimental packs that this was formed more abundantly when the hominy was not scrubbed, other conditions being equal.

2—Some grains may become black where they are against the can; at first just a little on a small area, but gradually more until a big portion of the grain is black. In the experimental packs, up to the present time, these grains always lie in a circle adjacent to the bottom seam or against the side seam. In some cases a complete circle has been observed on the bottom. These facts make it appear that the iron for the formation of the black discoloration of hominy comes first from the tin plate where its physical condition has been altered by bending or cutting. If this is true for hominy it seems likely that the iron acquired by other products from the container probably comes first and perhaps largely from these regions.

This clear-cut picture is never met in a commercial can of hominy, as a result of its being handled in transportation and in trading. The first form of black is of little consequence because it is washed off frequently enough and so finely distributed in the can that it is seldom serious. The black grains, however, make it unfit for the trade, not from the standpoint of wholesomeness, but of appearance.

It is not to be concluded that black discoloration would not occur if a can could be made without sharp bends or without the tin plate having undergone some strain. Under such circumstances the formation of black might be retarded but it would be likely to occur within the period of manufacture and consumption of a pack. It is known that the tin on tin plate does not form a complete and continuous coating. Every type of tin container has in it one or both of the conditions of a fractured tin coating, a strain in the plate due to bending or the cut edge of the plate exposed. In the case of the sanitary double seam, the lock side seam, and the expansion rings, the tin coating is more or less broken. In the lap side seam a cut edge of the plate is exposed. This is also true on the end and around the hole of the hole and cap cans.

The Determination of Carbon Dioxide in Self-Rising Flour[1]

By Benjamin R. Jacobs[2]

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The following method of determining carbon dioxide by absorption in barium hydroxide has given very satisfactory results with self-rising flour. Contamination with atmospheric carbon dioxide is avoided by aspirating CO_2-free air through the apparatus, by working rapidly, and by keeping apparatus and reagents properly stoppered. The titration must be carried to a definite end-point.

In consideration of the enormous increase in the production of self-rising flours and of the large number of millers who are manufacturing them practically without chemical control, it seems desirable to present a rapid and accurate method of determining carbon dioxide in this product.

Since the determination of carbon dioxide is made for a large variety of purposes, many methods and many forms of apparatus have been devised. Some require very elaborate apparatus and precautions, and the sources of error are many. Truog[3] determined carbon dioxide in certain soil investigations by the alkali titrimetric method, using measured amounts of barium hydroxide, in which the carbon dioxide was precipitated as barium carbonate which is practically neutral to phenolphthalein. The excess of barium hydroxide was determined by titration and the amount of carbon dioxide by difference.

The Truog method has been adapted by Gurgar[4] to the determination of carbon dioxide in plant respiration studies. The apparatus used by Gurgar is more elaborate than that of Truog, but it is also susceptible of greater accuracy, owing to the use of more dilute reagents, as well as to the precautions used against exposing the standard barium hydroxide solution to the atmosphere.

In determining carbon dioxide in self-rising flours the tendency of the sample to lump when treated with water must be overcome; otherwise small lumps of dough containing dry flour in the center will cause errors in the determination. It has been found that this may be overcome by adding only enough water to form a thick paste, the amount required being about three times the weight of the sample. Vigorous shaking is necessary to break up the lumps and form a homogeneous paste.

APPARATUS

The apparatus shown in the accompanying figure consists of a tower, A, a flask, B, of 1000-cc. capacity, a 300-cc. round-bottomed flask, D, provided with a 100-cc. separatory funnel, C, and a glass bulb, E, connected with two 16-oz. bottles, F, filled with 50 per cent sodium hydroxide solution and perforated or solid glass beads, G.

REAGENTS

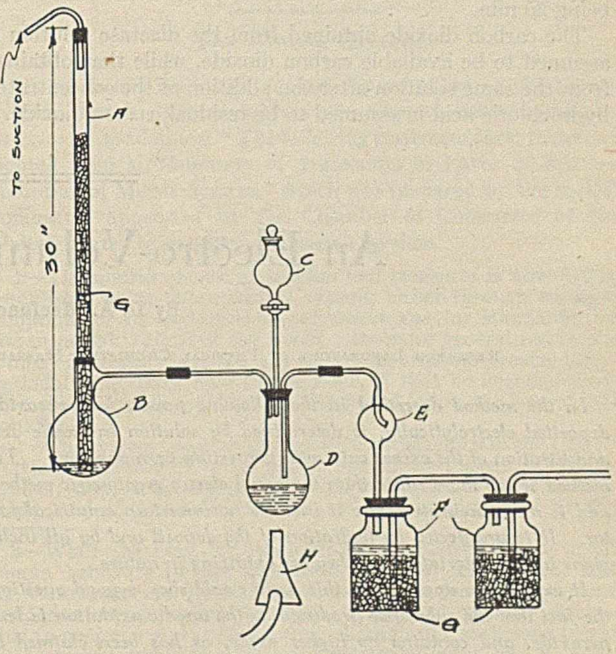
STANDARD HYDROCHLORIC ACID—A 0.1 N solution is used.

BARIUM HYDROXIDE—Seven g. of $Ba(OH)_2$ are dissolved in 1 liter of boiling water and filtered into a stock bottle which has been freed from carbon dioxide. A double filter paper is used and the funnel is never allowed to run dry until the solution has all gone through. Fifty cc. are used for each determination. About 19 cc. of 0.1 N HCl are required to neutralize this amount of barium hydroxide.

PHENOLPHTHALEIN—One gram of phenolphthalein is dissolved in 100 cc. of 95 per cent ethyl alcohol. Four drops are used for each determination.

CO_2-FREE WATER—This may be made either by passing CO_2-free air through water for 30 min. or by boiling for 15 min.

DIASTASE SOLUTION—This is made by dissolving 1 g. of diastase in a liter of CO_2-free water. 100 cc. are used for each determination. This solution should be made up fresh every day.



PROCEDURE

Fifty cc. of the barium hydroxide solution are introduced into flask B through the tower A, the apparatus having previously been freed of CO_2 by drawing CO_2-free air though it for 20 min. Approximately 5 g. of the flour to be tested are weighed in a test tube and dumped into dried flask D, which is immediately corked for future use or connected with the rubber stopper provided with the separatory funnel C. Air is then passed through at the rate of about four bubbles per second. One hundred cc. of the standard diastase solution are run into the separatory funnel. Approximately 15 cc. of this solution are introduced into the flask containing the sample and shaken gently until a homogeneous paste is obtained, whereupon the remaining portion of the diastase solution is introduced. Flask D is immersed in a dish containing water at 70° C. for about 10 min. in order to hasten the action of the diastase on the starch. The temperature of the water in the dish is then increased to boiling, the flask is shaken occasionally, and the determination continued for a total of 25 min. Just before the end of this time a flame is applied directly to the bottom of the flask and the contents are brought to a boil for a few seconds. This should be done carefully to avoid charring.

When the determination is completed the section is closed off with a stopcock connected to the tubing above the tower. The apparatus is disconnected at the side tube of the flask

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[1] Received January 18, 1922.

[2] Director, National Cereal Products Laboratories.

[3] This Journal, 7 (1915), 1045.

[4] *Plant World*, **20**, 288.

B. The tower is raised a few inches, and the beads are allowed to slide out. It is then washed with a little CO_2-free water. The washing is done quickly and if the flask is then corked or the titration made immediately there is scarcely any possibility of contamination from the air. The barium hydroxide solution may be titrated by adding four drops of phenolphthalein indicator. Titrate with hydrochloric acid to the permanent disappearance of the last traces of pink color. If it is desired to determine the residual CO_2 in the sample, flask B and tower A are immediately replaced by another similar flask and tower, which have been previously freed from CO_2 and contain 50 cc. of barium hydroxide solution. Five cc. of concentrated hydrochloric acid are added through the separatory funnel C to the flask containing the sample. The solution is then brought to a boil and the boiling continued very gently, the total time of aspiration being 25 min.

The carbon dioxide obtained from the diastase solution is assumed to be available carbon dioxide, while that obtained from the same solution after the addition of the concentrated hydrochloric acid is assumed to be residual carbon dioxide.

Accuracy of Method

The accuracy of the above method and the efficiency of the apparatus and technic in preventing contamination of the reagents by the carbon dioxide of the air were tested by using measured quantities of standard barium hydroxide in the regular way in the tower and passing CO_2-free air through it for 25 min.

A number of blank determinations were made on commercial grades of flour. In no case was there found to be more than 0.008 per cent of total carbon dioxide, while in several instances the blanks were nil. The method was also tried by using ordinary flour containing no added carbon dioxide and adding known quantities of baking powder of known composition. The baking powder used was a sample which has been used in collaborative work by the Association of Official Agricultural Chemists. It had been tested by five chemists and showed an average of 16 per cent total CO_2. In one instance the sample tested contained 24 mg. of total carbon dioxide and there were recovered 23.60 mg. In another instance the sample analyzed contained 48 mg. of carbon dioxide and there were recovered 46.56 mg.

An Electro-Volumetric Method for Lead[1,2]

By D. A. MacInnes[3] and Eric B. Townsend

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In the method described in the following paper, lead peroxide, deposited electrolytically, is determined by solution in oxalic acid and titration of the excess acid with potassium permanganate. The method seems more rapid than the usual electro-gravimetric method, and is more accurate, since it involves no uncertain empirical factor. It is unaffected by hydration of the deposit and by all inclusions in the material unless they are oxidizing in nature.

It would also appear that this work establishes, beyond question, the fact that the substance produced by the anodic oxidation is lead peroxide, and contains no higher oxide, as has been claimed by several authors.

In a study of the reactions occurring in the lead accumulator,[4] one of the authors, with his associates, showed that the product of the oxidation of lead at an anode is PbO_2, and not a mixture of this substance with a higher oxide, as has been claimed by Féry[5] and others. However, in the usual electrolytic determination of lead, in which the metal is determined by weighing the dried peroxide, it has been found necessary to use an empirical factor, smaller than the stoichiometrical factor, 0.8663. A low factor may be due to contamination with a higher oxide, or to a persistent hydration of the deposit. For the practical purpose of determining lead, this would not be of importance if there were certainty as to the value of this factor. Hollard,[6] who believes that the discrepancy between the factor for pure PbO_2 and that observed experimentally is due to a higher oxide, obtained values, with a polished anode, varying from 0.740 for small amounts of lead to 0.861 for large amounts. With a roughened electrode he obtained the average value 0.853 for all amounts of oxide, but his experimental deviations were ±0.005 from this factor. Treadwell,[7] on the other hand, recommends a *high* value of the factor, 0.886, for small amounts of oxide, and a lower one, 0.863, for larger quantities. This is far from being a summary of the work on this subject, but it is sufficient to indicate that there is considerable uncertainty as to the value of the factor.

It occurred to the writers that the oxidizing power of the deposited peroxide, on an excess of oxalic acid for instance, could be made the basis for a convenient method of determining lead. Strangely enough, this rather obvious method has received practically no attention. A search through the journals and textbooks disclosed just two references to the method as a possibility and no evidence that it has been tried. Treadwell[8] says, "In a large excess of oxalic acid the lead peroxide (dried at 200°) goes very slowly into solution. The titrimetric determination of the peroxide is, therefore, slow and not to be recommended." Further, Scott[9] suggests such a method, but he states, in a personal communication, that he has not put it to actual test. It was, therefore, considered desirable to try the oxidizing property of the deposited oxide as a means of determining lead.

After some preliminary experiments with a gauze anode, it was found that the best deposits for this purpose were obtained with an anode consisting of a platinum dish, 9 cm. in diameter, roughened on the inside, and a platinum disk, rotating at about 600 r. p. m., as cathode. Small pieces of sheet lead were carefully cleaned and weighed, and dissolved in the anode dish, with 10 cc. of concentrated nitric acid and 15 cc. of water. The sheet lead was kindly furnished by the Bureau of Standards and contained impurities amounting to not more than 0.04 per cent. The resulting solution was electrolyzed with a current of about 12 amp., until the solution gave no test for lead, which was usually after about 30 min. The deposit was then washed with a little distilled water.

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[1] Received January 19, 1922.

[2] Published as Contribution No. 144 from the Research Laboratory of Physical Chemistry, M. I. T.

[3] Associate Professor of Physicochemical Research, M. I. T.

[4] MacInnes, Adler and Joubert, *Trans. Am. Electrochem. Soc.*, **37** (1920), 641.

[5] *Lumière élec.*, **34** (1916), 305; *J. Phys.*, **6** (1916), 21.

[6] *Bull. soc. chem.* **29** (1903), 151; **31** (1904), 239.

[7] "Electro-analytische Methoden," 148.

[8] *Loc cit.*, 150.

[9] "Standard Methods of Chemical Analysis," 240.

At this point, instead of drying and weighing, the peroxide was determined by one of two methods: (*a*) treatment with potassium iodide and titration of the liberated iodine with sodium thiosulfate, and (*b*) solution in an excess of standard oxalic acid and titration with potassium permanganate of the excess oxalic acid remaining after the reaction. These procedures will be discussed separately.

The Iodometric Method

The procedure followed was that described by Treadwell and Hall[10] for determining lead peroxide. About 0.6 g. of potassium iodide and small amounts of acetic acid and sodium acetate, dissolved in 25 cc. of water, were placed in the anode dish before the deposit had been allowed to dry. It was found, however, that the deposit dissolved very slowly and then only by constant rubbing with a glass rod. From 1.5 to 2 hrs. were necessary for the solution. Heating of the mixture to hasten solution was not advisable because iodine would undoubtedly vaporize to a certain extent. The liberated iodine was titrated with sodium thiosulfate which had been standardized in the usual manner against the potassium permanganate solution described below. Some results of this procedure are given in Table I.

Table I—Iodometric Determination

	Time of Deposition Min.	Current Amp.	Wt. of Lead Grams	Wt. of Lead Determined Grams	Error Per cent
Expt. 1	32	12.4	0.0846	0.0843	−0.4
Expt. 2	40	13	0.2004	0.2000	−0.2

The low results are undoubtedly largely due to the difficulty of getting the deposit completely into solution in the mixture used. This procedure does not seem to be adapted to practical use.

The Oxalic Acid Method

An excess of standard oxalic acid (about 25 cc. of 0.1 *N*) together with 5 cc. of concentrated nitric acid were placed on the peroxide deposit before it had been allowed to dry. The solution was heated to about 80°, until the solid had completely dissolved, which took about 5 min. It is important to keep the volume of the solution as small as possible, as the accuracy of the permanganate titration is greater when using concentrated solutions. After the solution had been transferred to a small beaker and a small amount of concentrated sulfuric acid had been added to precipitate the lead, the excess of oxalic acid was titrated with permanganate solution which had been standardized against pure dry sodium oxalate. The burets and weights used had been carefully calibrated. Some results obtained by this method are outlined in Table II.

Table II—Oxalic Acid Method

			Weight of Lead		
Expt.	Current Amp.	Time of Deposition Min.	Taken Grams	Found Grams	Error Per cent
1	13.0	45	0.0889	0.0888	−0.11
2	13.0	40	0.0906	0.0904	−0.22
3	12.0	35	0.1604	0.1606	+0.12
4	12.2	30	0.1793	0.1792	−0.06
5	11.8	32	0.1772	0.1773	+0.06
6	12.6	30	0.1867	0.1868	+0.05
7	11.0	41	0.2113	0.2115	+0.10
8	12.2	30	0.1939	0.1938	−0.05

This combined electrolytic and volumetric method appears to be more rapid than the usual electro-gravimetric determination, and is certainly more accurate, since it involves no uncertain empirical factor. There does not seem to be any observable difference in accuracy when large and small amounts of lead peroxide are deposited, which indicates that the variation in the empirical factor considered above is probably due to differences in hydration rather than to variation in the chemical nature of the deposit. The determination is unaffected by hydration of the deposit, and by all inclusions in that material, unless they are oxidizing in nature. It has, of course, all of the advantages of the electrolytic method. "By this (electrolytic) method the lead is separated from zinc, cobalt, nickel, iron, aluminium, copper, gold, mercury, antimony, and cadmium. Traces of silver and bismuth, if present, are deposited as peroxides with the lead."[11]

Further, this work is in accord with the results of the experiments on the lead accumulator, referred to above. It appears to establish definitely the fact that the product of the anodic oxidation of lead is lead peroxide, which contains no higher oxides.

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[10] "Quantitative Analysis," 675.

[11] Olsen, "Quantitative Chemical Analysis," 222.

The Metric System

So much has been said against the adoption of the metric system that it appears desirable to advance some arguments in favor of its adoption. The following statements are, therefore, quoted from a "Summary of Arguments in Favor of Further Adoption of Metric System," which was prepared by the special committee appointed by the Chamber of Commerce of the United States to consider the metric system.

1—The metric system of weights and measures is now firmly established as an international system, either through its legal adoption, or its exclusive or permissive use for standards, by the principal nations of the world. Its more general use in the United States is therefore advocated to promote greater international uniformity, and in the hope, if that be accomplished, that other English-speaking peoples would follow the lead of this country.

2—The system has been proved to be satisfactory in the United States and elsewhere in its use in complicated scientific calculations; and, in the metric countries, adaptable to the everyday trade, and to industrial and educational requirements of the people.

3—While the basis for the units of the metric system is, of course, arbitrary, it has now been definitely established, and the various decimal gradations give a wide choice for convenient designated measurements of length, weight and capacity, adaptable to common and scientific use. Familiarity with such terms as the pound and inch is largely a matter of habit, and it is believed that habit would also make the use even of the decimal subdivisions of the metric system, such as the millimeter, equally familiar and convenient.

4—The basic simplicity of the system, with its few units, as the meter, liter, gram, with decimal subdivisions, makes both teaching and learning easy; and, in trade, makes billing and computation simple. During the period of transition, when there would for a time be more active dual relations than at present, conversion would be almost automatic through the use of tables of equivalents.

5—An arbitrary imposition of any system of weights and measures, without a reasonable period of transition or the principle of exemption, where desirable for manufacture or for export to nonmetric countries, might be a hardship. A gradual change has been effected in most metric countries, and it is believed that such change was accomplished without hardship and without such heavy expense as claimed by those opposed to its adoption. It is also believed that greater conformity to the habits of metric countries would tend to increase our export trade. The question of countervailing imports of manufactured goods and raw material is an economic subject quite apart from the question at issue.

6—The relative international popularity of the two major systems in use is shown by the number of nations which in recent years have adopted the metric system, while none has formally adopted the British-American system, although in population the two groups are about equal. [Since 1914, Poland, Latvia, Russia, Japan, Haiti, and Esthonia have become metric.]

A pamphlet entitled "Uehling CO_2 Equipment" has been prepared by the Uehling Instrument Company for guiding the engineer and fireman in reducing the waste of fuel up the chimney.

The Determination of Bromide in Brines and Mineral Waters[1]

By C. C. Meloche[2] and H. H. Willard[3]

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A detailed study has been made of the various factors affecting the separation of bromine from very large amounts of chloride by oxidation with excess of permanganate and a carefully regulated amount of hydrochloric acid. The bromine containing a little chlorine after absorption in alkali is reduced and precipitated with silver. The mixed silver halides are fused in chlorine and from the loss in weight the amount of bromine is calculated.

If iodide is present it is first oxidized to iodate by permanganate in alkaline solution, after which the bromine is distilled off as usual. The iodate remaining may be determined by titration with thiosulfate.

The method as finally recommended is accurate and more rapid than other methods of equal accuracy. It is suitable for brines and similar substances and very large samples can be used.

The accurate quantitative determination of small amounts of bromide in the presence of large amounts of chloride has always been a matter of considerable difficulty. Most of the methods hitherto suggested seek, by regulation of the acidity or choice of the oxidizing agent or both, to arrange conditions so that the bromine can be liberated and distilled off while the chlorine remains in the residue as chloride. A satisfactory separation is possible when the concentration of chloride is low, but high concentration of chloride renders the quantitative separation of small amounts of bromine in one operation almost impossible. For this reason, it is advisable to carry out a preliminary concentration process with a strong oxidizing agent and a strong acid, making certain that the bromine is entirely recovered along with some chlorine. The bromine in the distillate can then be determined with precision.

The method recommended is briefly as follows: The sample of brine, somewhat diluted if necessary, is treated with an excess of permanganate and hydrochloric acid, heated, and the bromine removed by means of a current of air. The bromine, together with some chlorine, is absorbed in sodium hydroxide solution, reduced to bromide and chloride, preferably by hydrazine sulfate, acidified with nitric acid, and precipitated by means of silver nitrate. The weight of bromine is calculated from the loss in weight of the mixed silver halides on ignition in chlorine.

A bibliography on the determination of bromine is given by Baughman and Skinner.[4] The work of Baubigny[5] is of particular importance in the present case.

Apparatus and Reagents

The apparatus used in this investigation (Fig. 1) consisted essentially of a 250-cc. steam-jacketed retort, A, a 10-bulb tube, B, a saturator, C, a flowmeter, D, a pressure regulator, E, and a source of pure compressed air.

The retort was provided with the air inlet tube, *a*, which was ground to fit and extended nearly to the bottom. The tubulus was bent at an angle of about 80° as shown. The slip joint between the tubulus and the 10-bulb tube was rendered gastight by means of a short piece of rubber tubing.

The air current before entering the retort passed through a soda-lime tower, not shown, through the regulator, the flowmeter, and the saturator. The regulator consisted of a long tube, *b*, connected with the main air line and dipping in water contained in a tall cylinder. By means of the screw pinchcock *c* the air supply was so regulated that a little was continually escaping through *b*. By adjusting the level of water in the cylinder the pressure could be fixed as desired, and in this way the rate of passage of the air could be maintained at any definite value up to 80 l. per hr. For high rates, the water in the cylinder was partly replaced by mercury. The rate of passage of the air was indicated by the flowmeter.

The saturator was a steam-jacketed, 250-cc. distillation flask containing 2 g. of sodium hydroxide dissolved in about 150 cc. of water. The inlet tube extended nearly to the bottom of the flask.

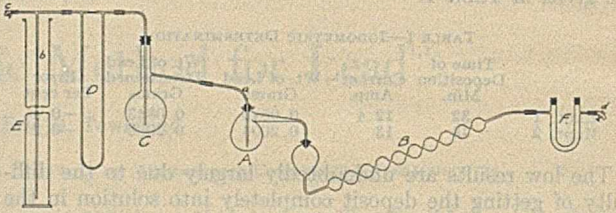

Fig. 1

The 10-bulb tube was of ordinary dimensions, each bulb being about 30 mm. in diameter and the constricted portions about 6.5 mm. in diameter.

The guard tube F, containing very dilute silver nitrate solution, a little hydrazine sulfate, and a few drops nitric acid, served to detect any loss of halogen.

The standard bromide solution was made by dissolving in distilled water specially purified potassium bromide.[6] The strength of the solution was determined by precipitation and weighing of fused silver bromide and also by determination of the loss in weight of the silver bromide on ignition in chlorine. The results obtained by the two methods were in close agreement, thus proving the absence of appreciable amounts of chloride. The weight of bromine per gram of solution was 0.015787 gram.

The sodium chloride which was added in large amounts was Kahlbaum's best grade. The other materials used were of chemically pure grade. When traces of bromide were present they were determined by blank analyses.

Procedure

In the experiments listed in Tables I to VIII the retort was charged with known weights of standard potassium bromide solution and of sodium chloride, the weighed excess of potassium permanganate was introduced, the solution diluted, and the hydrochloric acid added last, the total volume being 150 cc. for all experiments. The air inlet tube was immediately inserted and the retort connected with the 10-bulb tube which contained 2 g. of sodium hydroxide dissolved in 70 cc. or more of water. After the entire apparatus was connected the air was turned on, and any slight adjustment in rate quickly made. The steam was then turned on under the saturator and under the retort, and the time noted. When the operation had continued the desired length of time, the air

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[4] This Journal, **11** (1919), 954.

[5] *Compt. rend.*, **125** (1897), 527; **128** (1899), 1160, 1236.

[6] Prepared by Dr. R. K. McAlpine for use in atomic weight work.

stream was interrupted most satisfactorily by means of a screw pinchcock at *d*. The steam and air supply were then turned off.

After the 10-bulb tube had been disconnected the hypobromite solution containing some hypochlorite was transferred to a 500-cc. glass-stoppered Erlenmeyer flask and reduced by adding a weighed excess of hydrazine sulfate and swirling the flask. The solution was then made approximately 0.2 *N* with nitric acid and the silver bromide, together with some silver chloride, precipitated and washed in the manner usually prescribed for careful work. The precipitate contained in a Gooch crucible supplied with a Rose cover, preferably of quartz, was first thoroughly dried at about 180°, then raised to a temperature somewhat above the fusion point for about 0.5 hr. After cooling and weighing, the precipitate was heated at the latter temperature in a current of chlorine for about 1 hr. with occasional tilting of the crucible. After cooling and weighing again, the operation was repeated, but usually without a noticeable loss in weight. It was found that when fine asbestos of high grade was used and excessive temperatures avoided, very satisfactory results could be obtained without transfer of the precipitate. In heating the Gooch crucibles to the higher temperature, an outer protecting dish was always provided. The amount of bromine was calculated from the loss in weight on ignition in chlorine by use of the factor 1.7976.

After preliminary determination of the approximate conditions necessary, the effect of each of the following factors was studied separately: (1) Duration of passage of air; (2) rate of passage of air; (3) concentration of permanganate; (4) concentration of hydrochloric acid; (5) the amount of chlorine carried over; (6) the concentration of sodium chloride; (7) the concentration of bromide; (8) the presence of iodide; (9) the character of the reducing agent; (10) the presence of other constituents of brine.

DURATION OF PASSAGE OF AIR

Experiments in which the duration of the passage of air was varied from 1.5 to 3 hrs. were run at a rate of 10 l. per hr. The results given in Table I show that when the rate is as low as 10 l. per hr., the recovery of bromine is scarcely quantitative in 3 hrs. It was later demonstrated (Table III) that the bromine could be entirely recovered in 30 min. if the rate of passage of the air was sufficiently increased.

TABLE I—EFFECT OF VARIATION IN DURATION OF PASSAGE OF AIR

Rate = 10 l. per hr.
NaCl present = 25.0 g.; $KMnO_4$ added = 1.0 g.; HCl added[1] = 0.40 g.; total volume of solution in retort, including reagents = 150 cc.

Duration of Passage of Air Hours	Bromine Present Grams	Bromine Found Grams	Error Grams
1.5	0.2586	0.2549	−0.0037
2.0	0.2609	0.2589	−0.0020
3.0	0.2586	0.2580	−0.0006

[1] This means actual HCl, although it was added in the form of a dilute solution.

RATE OF PASSAGE OF AIR

The effect of increasing the rate of passage of the air is illustrated by the experimental results given in Table II. At the higher rates, the recovery is more nearly complete in a given length of time. With 10-bulb tubes of ordinary dimensions the rate can be increased to 80 l. per hr. without appreciable loss of bromine. This fact makes possible the complete recovery of bromine in 30 min., as shown in Table III. At rates above 80 l. the accumulation of liquid in the end bulbs is likely to be so rapid that mechanical loss occurs before the end of the experiment; 70 l. per hr. is a convenient rate for accurate work.

TABLE II—EFFECT OF INCREASE IN RATE OF PASSAGE OF AIR
(Conditions same as given under Table I)

Rate of Passage of Air L. per Hr.	Duration of Passage of Air Min.	Bromine Present Grams	Bromine Found Grams	Error Grams
10	120	0.2609	0.2589	−0.0020
20	120	0.2589	0.2580	−0.0009
30	120	0.2583	0.2576	−0.0007
30	60	0.2583	0.2574	−0.0009
40	60	0.2584	0.2580	−0.0004

TABLE III—EFFICIENCY OF RECOVERY OF BROMINE AT HIGHER RATES OF PASSAGE OF AIR

NaCl present = 25.0 g.; $KMnO_4$ added = 0.5 g.; HCl added = 0.3 g.; total volume of solution in retort, including reagents = 150 cc.

Rate of Passage of Air L. per Hr.	Duration of Passage of Air Min.	Bromine Present Grams	Bromine Found Grams	Error Grams
50	30	0.2594	0.2585	−0.0009
60	30	0.2579	0.2578	−0.0001
70	30	0.2591	0.2590	−0.0001
80	30	0.2588	0.2589	+0.0001

CONCENTRATION OF PERMANGANATE

When bromine is liberated by means of an excess of potassium permanganate in hot, slightly acid solution, the permanganate is reduced for the most part to manganese dioxide. If the theoretical amount or only a slight excess of permanganate is used the recovery of bromine is incomplete, as shown in the last experiment, Table IV. No trouble is experienced, however, when a moderate or even a rather large excess is employed as in the first three experiments. Sufficient permanganate has been added if at the end of the distillation the liquid in the retort still retains a deep purple color. For amounts of bromine up to 0.26 g., 0.5 g. of potassium permanganate is recommended.

TABLE IV—EFFECT OF CHANGE OF CONCENTRATION OF POTASSIUM PERMANGANATE

Rate of passage of air = 40 l. per hr.; duration of passage of air = 1.0 hr. NaCl present = 25.0 g.; HCl present = 0.4 g.; total volume of solution in retort, including reagents = 150 cc.

$KMnO_4$ Added Grams	Bromine Present Grams	Bromine Found Grams	Error Grams
5.0	0.2585	0.2583	−0.0002
1.0	0.2584	0.2580	−0.0004
0.5[1]	0.2581	0.2580	−0.0001
0.2[2]	0.2578	0.2565	−0.0013

[1] Permanganate almost entirely reduced.
[2] Permanganate entirely reduced.

CONCENTRATION OF ACID

Increase in the concentration of hydrogen ion favors the liberation of bromine but at the same time favors the liberation of chlorine. The concentration of acid must therefore be carefully regulated if an exact separation is being attempted. Under these conditions, however, there is danger that the bromine may not be entirely recovered. The authors have therefore used a strong acid, as hydrochloric acid, in such amounts that a little chlorine is liberated along with the bromine. The recovery of all the bromine is insured and the small amount of chlorine carried over does no harm. Upon examination of Table V, it will be observed that when a moderate excess of acid is used the results are very satisfactory but when a slight excess only is employed as in the fourth experiment, the results are far from quantitative. From 0.3 to 0.4 g. of actual hydrochloric acid is recommended when the amount of bromine present does not exceed 0.26 g.

TABLE V—EFFECT OF CHANGE IN CONCENTRATION OF HYDROCHLORIC ACID

Rate of passage of air = 40 l. per hr.; duration of passage of air = 1 hr. NaCl added = 25.0 g.; $KMnO_4$ added = 0.5 g.

HCl Added Grams	Bromine Present Grams	Bromine Found Grams	Error Grams
0.4	0.2594	0.2592	−0.0002
0.3	0.2587	0.2588	+0.0001
0.2	0.2589	0.2585	−0.0004
0.16	0.2589	0.2508	−0.0081

CHLORINE IN DISTILLATE

The amount of chlorine carried over in the course of removal of the bromine increases with increase in concentration of hydrogen ion and of the oxidizing agent. When these factors remain constant, the amount of chlorine carried over decreases with increase in the concentration of bromide, as shown by the first three experiments in Table VI. Even the maximum amount, which in any case does not much exceed 0.2 g., exerts no harmful effect. The only additional information needed for the determination of chlorine in the distillate is the weight of the empty crucible, which is not ordinarily obtained if bromine alone is required. The chlorine derived from the sodium hydroxide should of course be subtracted. In each experiment given the recovery of bromine was quantitative, as shown in Table VIII.

TABLE VI—WEIGHT OF CHLORINE IN DISTILLATE AS AFFECTED BY CONCENTRATION OF BROMIDE

Rate of passage of air = 70 l. per hr.; duration of passage of air = 30 min., except in last experiment, where it was 45 min.

NaCl present = 25.0 g.; total volume of solution, including reagents = 150 cc.

HCl Added Grams	$KMnO_4$ Added Grams	Bromine Present Grams	Chlorine in Distillate Grams
0.3	0.5	0.0000	0.2082[1]
0.3	0.5	0.0108	0.1457
0.3	0.5	0.0522	0.1020
0.6	1.0	0.5154	0.2145
0.6	1.0	0.5148	0.2138

[1] Average of two determinations.

CONCENTRATION OF SODIUM CHLORIDE

The presence of large amounts of sodium chloride retards very noticeably the separation of bromine. Conditions which are satisfactory for the quantitative recovery of bromine when other salts are present in low concentration may prove entirely inadequate when the concentration of other substances is high. Having observed this fact in preliminary work, practically all experiments have been conducted with sodium chloride present in high concentration in order that the conclusions reached may be safely applied to brine analysis. The retardation of the evolution of bromine when a high concentration of sodium chloride exists is due probably to the formation of perhalide and to the lowering of the vapor tension. The results given in Table VII show the amount of discrepancy observed. Low results had previously been obtained in the case of Expt. 1 because of insufficient permanganate, in the case of Expt. 3 because of insufficient acid, and in the case of Expt. 5 because of the low rate of passage of air, but in every case the repetition of the experiment with 1.0 g. instead of 25.0 g. sodium chloride showed a material improvement in the recovery of bromine.

TABLE VII—EFFECT OF HIGH CONCENTRATION OF SODIUM CHLORIDE

Total volume of solution, including reagents = 150 cc.

Expt.	$KMnO_4$ Added Grams	HCl Added Grams	Duration of Passage of Air Hrs.	Rate of Passage of Air L. per Hr.	NaCl Present Grams	Bromine Present Grams	Bromine Found Grams	Error Grams
1	0.2	0.4	1.0	40	25	0.2578	0.2565	−0.0013
2	0.2	0.4	1.0	40	1	0.2576	0.2572	−0.0004
3	0.5	0.16	1.0	40	25	0.2589	0.2508	−0.0081
4	0.5	0.16	1.0	40	1	0.2601	0.2538	−0.0063
5	1.0	0.4	2.0	10	25	0.2609	0.2589	−0.0020
6	1.0	0.4	2.0	10	1	0.2603	0.2593	−0.0010

CONCENTRATION OF BROMIDE

Since the bromine content of brines and bitterns may vary considerably, it is important that the method used should have a wide range of application. The results given in Table VIII were obtained with amounts of bromine varying from 0.01 to 0.50 g. The conditions were chosen so as to duplicate as nearly as possible those recommended by the authors for an actual brine analysis. It will be noted that the errors are small and the method very accurate. It is more convenient to work with samples containing 0.25 g. of bromine or less, but a larger amount of bromine, *e. g.*, 0.5 g., may be present, providing the requisite excess of hydrochloric acid and of potassium permanganate is added and the ignition in chlorine continued somewhat longer.

TABLE VIII—EFFECT OF VARYING CONCENTRATION OF BROMIDE

Rate of passage of air = 70 l. per hr.; duration of passage of air = 30 min., except in last experiment, which was run for 45 min.; NaCl present = 25.0 g.

HCl Added Grams	$KMnO_4$ Added Grams	Bromine Present Grams	Bromine Found Grams	Error Grams
0.3	0.5	0.0000	0.0003	+0.0003
0.3	0.5	0.0108	0.0108	0.0000
0.3	0.5	0.0522	0.0521	−0.0001
0.3	0.5	0.2591	0.2590	−0.0001
0.6	1.0	0.5154	0.5157	+0.0003
0.6	1.0	0.5148	0.5150	+0.0002

PRESENCE OF IODIDE

The amount of iodide present in a natural brine is often so small that it may be disregarded, especially if the permanganate is added first to the neutral solution and the acid added last. If desired, the iodine can be distilled over with the bromine. In this case the acid is added first and the permanganate last, to avoid oxidation to iodate. The iodine is then determined in a separate sample and the proper correction applied to the loss in weight on ignition in chlorine before the bromine is calculated. When significant amounts of iodide are present the bromine may be directly determined and the necessity for the determination of iodine avoided by the following modification:

The sample of brine is made distinctly alkaline, treated with an excess of permanganate, and boiled to convert iodide to iodate. After cooling, the customary excess of acid is added and the determination finished as usual. If an excess of permanganate is present during the entire operation the iodine remains in the form of iodate and the interference of iodide is effectively eliminated, as the results in Table IX show.

TABLE IX—EFFECT OF PRESENCE OF IODIDE ON DETERMINATION OF BROMINE

Rate of passage of air = 70 l. per hr.; duration of passage of air = 30 min.

NaCl present = 20.0 g.; wts. $KMnO_4$ and HCl calculated as explained above.

Iodine Present Grams	Iodine Found Grams	Error Grams	Bromine Present Grams	Bromine Found Grams	Error Grams
0.0659	0.0655	−0.0004	0.2582	0.2585	+0.0003
0.1243	0.1250	+0.0007	0.2572	0.2575	+0.0003

The experiments there given were conducted as follows: The neutral solution containing bromide, iodide, and a large excess of chloride was treated with sufficient sodium hydroxide (about 0.1 g.) so that the green color of the manganate developed when the permanganate was added in the cold. The amount of potassium permanganate added was slightly more than the weight calculated to oxidize iodide to iodate plus the usual 0.5 g. for the liberation of bromine. After boiling for 2 min. the solution was cooled and an amount of hydrochloric acid, slightly more than sufficient to neutralize the added alkali and the alkali formed on reduction of the permanganate by iodide, was introduced, in addition to the 0.3 g. of hydrochloric acid usually used. After diluting to 150 cc. the bromine was removed by a current of air in the usual way.

The residue in the retort was used for the determination of iodine by the method of Baughman and Skinner,[7] modified as follows: The solution after dilution was treated with sufficient sodium peroxide to reduce the permanganate, boiled for 10 min. or more to remove any excess of peroxide, and filtered from the precipitate of manganese dioxide. The iodine which remained in the form of iodate was determined

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[7] THIS JOURNAL, 11 (1919), 563.

by adding the neutralized solution to an excess of potassium iodide solution containing hydrochloric acid. The liberated iodine was titrated with standard sodium thiosulfate in the usual manner. Since six atoms of iodine are liberated for every atom of iodine originally present, the method is well adapted for the determination of small amounts of iodine.

Reducing Agent

The quantitative absorption of bromine vapor from its mixture with air by means of dilute alkali presents no difficulties whatever, as shown in discussing the rate of passage of air. The resulting solution, however, contains hypobromite and hypochlorite which must be reduced before the ordinary gravimetric method can be applied. In the experiments previously described reduction has been accomplished by means of hydrazine sulfate. This reagent is ideal in almost every respect. It reduces hypobromite, hypochlorite, bromate, and chlorate almost instantaneously in the cold. The excess is without reducing action on silver nitrate or dilute nitric acid and therefore need not be removed. It is easily purified by recrystallization. The substance is, however, somewhat expensive and not always obtainable.

Of the more common reducing agents, sodium peroxide and possibly ammonium hydroxide are preferable to sulfurous acid which is sometimes used. Boiling is required in both instances and the solution must be cooled again before nitric acid can be added. Neither of the reagents is effective for the reduction of bromates and chlorates, should these be present. The results given in Table X were obtained when these reagents were substituted for the hydrazine sulfate. For the first experiment 2.0 g. of sodium peroxide were slowly hydrated, then added to the hypobromite-hypochlorite mixture and the alkaline solution boiled for 15 min. In the second experiment an excess of ammonium hydroxide was added and the solution boiled for 5 min.

Table X—Efficiency of Other Reagents for Reduction of Hypobromite

(Conditions otherwise the same as for first four experiments, Table VIII)

Reagent	Bromine Present Grams	Bromine Found Grams	Error Grams
Na_2O_2	0.2577	0.2577	0.0000
NH_4OH	0.2581	0.2574	−0.0007

Effect of Other Constituents of Brine

To learn the effect of other constituents of brine, synthetic brines were prepared containing large amounts of sodium chloride, calcium chloride, and magnesium chloride together with a small amount of ferric chloride and a carefully determined weight of potassium bromide. During analysis the rate of evolution of chlorine and bromine was noticeably increased, as a result of the catalytic effect of ferric chloride. To avoid a slight loss at the beginning of the operation, the saturator was not heated for the first 5 or 10 min. The determination of bromine gave very satisfactory results, as shown in Table XI.

Table XI—Determination of Bromine in Synthetic Brine

Other constituents: $NaCl$ = 20.0 g.; anhyd. $CaCl_2$ = 2.5 g.; anhyd. $MgCl_2$ = 2.5 g.; anhyd. $FeCl_3$ = 0.048 g.; other conditions same as for first four experiments, Table VIII

Bromine Present Grams	Bromine Found Grams	Error Grams
0.2573	0.2568	−0.0005
0.2101	0.2098	−0.0003

The presence of considerable calcium and magnesium is ordinarily without marked effect, as the experimental results show, but when significant amounts of iodide are also present and it is desired to use the modification previously described, complications are introduced. When the solution is made alkaline preparatory to the oxidation of iodide to iodate, the mixed precipitate of magnesium hydroxide, calcium hydroxide, and calcium carbonate obtained is inconveniently bulky. If sufficient alkali is added to precipitate only part of the magnesium, loss of bromine is likely to occur on boiling. Under these conditions it is advisable to remove the iron, calcium, and magnesium as explained below.

Determination of Bromine in Natural and Artificial Brines

procedure in absence of iodides—A sample of brine containing not more than 0.3 to 0.5 g. of combined bromine, and in any case not more than 100.0 g. of concentrated brine, is transferred to the retort. According to the amount of bromine present, 0.5 to 1.0 g. of potassium permanganate is added in the cold. Before adding the acid the 10-bulb tube is charged with a solution containing 2.0 g. of sodium hydroxide "from sodium" in 80 cc. of water and the apparatus is otherwise placed in readiness. Hydrochloric acid (best in the form of a dilute solution) is added to the brine in sufficient amount to provide 0.3 to 0.6 g. of free HCl, depending on the amount of bromine present. After dilution to 150 cc., the apparatus is immediately connected up and the analysis finished as already described.

procedure when iodides are present—A sample of brine containing at the most 0.5 g. of combined bromine, 0.2 g. of combined iodine, and such amounts of iron, calcium, and magnesium that the removal of these elements can be conveniently accomplished, is diluted and treated hot with an excess of sodium hydroxide and sodium carbonate. After filtration and washing the filtrate is neutralized, concentrated to 100 cc., made alkaline to the extent of 0.1 g. of free sodium hydroxide, and transferred to the retort. A slight excess of potassium permanganate above that required to oxidize iodide to iodate plus the usual 0.5 to 1.0 g. is added in the cold without stirring. If the green color of manganate develops, conditions are satisfactory for the complete oxidation of iodide to iodate. If the green color does not appear, either the concentration of iodide is very low or insufficient alkali has been added. The odor of halogen indicates that insufficient alkali is present. The solution is boiled for 2 min., noting the odor at first to make sure that no halogen is lost, then cooled. Sufficient hydrochloric acid is added to provide the usual 0.3 to 0.6 g. of free HCl and the analysis finished as above directed. As much as 100 g. of strong brine may be used as a sample, providing the conditions as first stated are complied with. If desired, the residue in the retort may be used for the determination of iodine as previously described.

Determination of Bromine in Mineral Waters

A sufficiently large volume of the mineral water should be evaporated to give a total bromine content of several milligrams, if possible. Larger volumes may be evaporated if greater accuracy is desired. The concentrated solution or the residue taken up with a little hydrochloric acid is then analyzed for bromine by the method above described for brines.

The Council of the Optical Society of America has decided to hold an optical instrument exhibit during the annual meeting of the Society at the Bureau of Standards, Washington, D. C., next October. To enable the exhibit committee to plan the space adequately and assign it equitably, it requests those interested to submit the following information: What instruments are offered for exhibition? How much floor space would be necessary? What additional facilities other than space will be needed? When the information is at hand the exhibit committee will notify the prospective exhibitors of the amount of space allotted to them, and will see that the general laboratory facilities necessary are provided. The exhibitors will instal their own exhibits and meet the expenses incident thereto.

Notes on the Analysis of Cast Bronze[1,2]

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Many of the observations which are noted in the following pages are known, but they merit repetition because they represent desirable procedures and precautions which are often ignored. The method of analysis which is given is based on work done at the Bureau of Standards and by the coöperating analysts. It embodies nothing that is new, but possesses merit in that it groups desirable procedures and takes into account the known sources of error.

MOST of the observations contained in this paper were made in connection with the analysis of the Bureau of Standards standard sample of Cast Bronze No. 52. This bronze was chill-cast in 1 in. × 12 in. × 24 in. slabs under the supervision of Mr. P. E. McKinney at the Naval Gun Factory, Washington, D. C., and subsequently machined and mixed at the Bureau. Preliminary analyses demonstrated that the mixed sample was remarkably uniform in composition and that it was free from arsenic and phosphorus. The general composition of the bronze was fixed by the Advisory Committee on Nonferrous Metals and the actual composition as determined at the Bureau and by the coöperating analysts is as follows: copper, 88.33; tin, 7.90; zinc, 1.89; lead, 1.52; antimony, 0.16; nickel, 0.13; and iron, 0.12. The following firms coöperated with the Bureau of Standards in its analysis:

The American Brass Co.
Bridgeport Brass Co.
Scovill Manufacturing Co.
The Ajax Metal Co.
National Lead Co.
Lumen Bearing Co.
Lunkenheimer Co.
The National Cash Register Co.
Crane Company
Ledoux and Co.
A. D. Little, Inc.
Pennsylvania Railroad System
C. B. & Q. Railroad Co.
Naval Gun Factory, Washington, D. C.

NOTES ON THE METHODS OF ANALYSIS

SEPARATION OF TIN AND ANTIMONY BY DIGESTION WITH NITRIC ACID—In this universally employed separation, the following observations are worthy of note:

(1) Hot digestion of the nitric acid solution of the alloy for 3 to 6 hrs. is desirable and it is imperative to keep the solution and the washing solution *boiling hot* throughout the filtering operation.

(2) Evaporation of the nitric acid solution to dryness followed by drenching and digestion with nitric acid is not necessary with alloys containing only tin or ten times as much tin as antimony. The operation does no harm, however, and is desirable with alloys of high antimony content, although in this case complete deposition of antimony is impossible.

(3) Other elements like phosphorus, arsenic and vanadium are quantitatively carried down with tin, provided the ratio of tin to these elements is high enough; in addition, the tin precipitate always carries down more or less of such other alloy constituents as iron, copper, zinc, and silicon.

(4) The complete separation of tin and antimony is often a matter of doubt, owing to such factors as the presence of considerable iron (over 0.25 per cent), the presence of considerable antimony, too short a digestion period, or the acceptance of a filtrate which is not crystal-clear.

DETERMINATION OF COPPER—(1) Equally good determinations are obtained by slow electrolysis and by rapid electrolysis in a solenoid apparatus or with rotating cathodes.

(2) Traces of copper (0.1 to 0.3 mg.) escape deposition in carefully conducted electrolyses and no advantage is ordinarily gained by redeposition. In fact a mechanical loss may result, if the first deposit is dissolved without using proper precautions.

(3) If tin or antimony in the ionic state is present in the electrolyte, it will be deposited to some extent with the copper and consequently the deposit should be examined for these elements.

DETERMINATION OF TIN—(1) Gravimetric determinations of tin as oxide average higher than determinations by other methods and require correction for antimony (and such other elements as phosphorus and arsenic) as separately determined, and for such contaminants as iron, copper, zinc, and silicon as obtained either by actual determination and deduction or by separation and reprecipitation of the tin and antimony.

(2) Stannic oxide and antimony tetroxide are very easily reduced and consequently all reducing gases must be very carefully excluded during the ignition, which is best performed in a porcelain crucible set in a hole in an asbestos shield. When so protected the oxides will stand the full blast.

(3) Ignited tin and antimony oxides can be conveniently put in solution by fusion in a platinum crucible (with occasional stirring with a short platinum rod) with fused borax followed by digestion of the cooled melt in warm, dilute hydrochloric acid. The solution can then be tested for impurities by treating the solution with an excess of potassium hydroxide and hydrogen sulfide.

(4) The electrolytic method affords erratic values, sometimes low, owing perhaps to the lack of a suitable test for complete deposition, and sometimes high, owing to inclusions; this latter effect is often corrected by "blank" electrolyses.

(5) The iodometric method yields excellent results, provided the iodine solution is standardized under like conditions against material of known tin content; the tin titer so obtained is higher than the theoretical. The method is also remarkably free from interfering factors, the ordinary alloy constituents, as well as antimony and arsenic, being without effect.

DETERMINATION OF ANTIMONY—(1) Gravimetric determinations of antimony as Sb_2O_4 or Sb_2S_3 tend to give high values, owing in part to the difficulty in completely removing contaminating impurities. As noted under the determination of tin, Sb_2O_4 is very easily reduced; Sb_2S_3 cannot be satisfactorily ignited in paper.

(2) An accurate and desirable method is the modified Low procedure (oxidation of antimony from the trivalent to the quinquevalent condition by permanganate in cold hydrochloric-sulfuric acid solution). The titer of the permanganate solution obtained by titration against a compound of known antimony content is higher than that obtained by calculation from the iron value. The only interfering substance encountered in ordinary materials is arsenic. Fortunately this is usually absent or present in such small amount that a satisfactory correction can be calculated from the amount present.

DETERMINATION OF LEAD—(1) The electrolytic method yields accurate results when but small amounts of lead are involved and when the electrolyte is free from such interfering substances as manganese and colloidal metastannic acid.

(2) The sulfate method is to be preferred when large amounts of lead are involved or when the electrolyte contains manganese or tin.

(3) There is no apparent advantage in precipitating lead as sulfate and then dissolving it in ammoniun acetate and reprecipitating as chromate or molybdate.

DETERMINATION OF ZINC—(1) Equally good results are obtained by the precipitation of ZnS from formic acid or 0.01 N sulfuric acid solutions.

(2) The precipitation of zinc sulfide or phosphate is incomplete in the presence of glyoxime reagent.

(3) The precipitation of zinc as phosphate must be made with diammonium phosphate in very weak acetic acid solution, and the solution must be kept warm until the phosphate becomes crystalline.

(4) The conversion of zinc sulfide to sulfate requires care in order to drive off excess sulfuric acid without loss of sulfur trioxide from the sulfate.

(5) The ignition of zinc sulfide to zinc oxide must be carried out at a low initial temperature until carbon is destroyed, lest there be a reduction and volatilization of zinc; a final temperature of 850° C. is required to convert completely to oxide the sulfate which is formed, and a temperature above 950° C. must be avoided on account of the volatility of zinc oxide.

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[1] Received February 3, 1922.

[2] Published by permission of the Director of the Bureau of Standards.

DETERMINATION OF IRON—(1) The greatest source of error lies in ignoring the iron which is always carried down by tin and antimony during a nitric acid attack; frequently all of the iron is carried down.

(2) In gravimetric determinations corrections should be applied for silica and the possibility of the presence of such elements as aluminium borne in mind.

(3) In volumetric work corrections as indicated in blank determinations should be applied. It is to be remembered that Jones reductors always give a greater blank in the first run after disuse for a short period, and that solutions which have been treated with hydrogen sulfide contain oxidizable polythionic acids which must be destroyed by permanganate before final reduction with zinc or stannous chloride.

DETERMINATION OF NICKEL—(1) For small amounts of nickel the glyoxime method is unquestionably the most desirable. The glyoxime should be added to the hot acid solution which is then made ammoniacal. This results in quicker precipitation with small amounts of nickel than is obtained by reversing the procedure and the precipitate is more easily filtered. Digestion of the warm solution for one to two hours before filtration is desirable and hot water is the most satisfactory wash.

(2) In case nickel dimethylglyoxime is ignited to the oxide, care must be taken to prevent sublimation of the undecomposed salt.

(3) The electrolytic method tends to give high values with small amounts of nickel, owing in part to solution of the anode and partial deposition of platinum on the cathode.

METHOD OF ANALYSIS

The most attractive method for the analysis of this type of material lies in a nitric acid attack followed by digestion and filtration to separate tin and antimony from the other elements. It is apparent, from what has been said, that the nitric acid filtrate must be examined for tin and antimony, while the nitric acid precipitate must be worked over for such contaminating elements as iron, copper, and zinc.

The following method calls for a nitric acid attack on two samples of bronze. In one sample, tin and antimony are filtered off, washed slightly, reserved, and then combined with any tin or antimony recovered from the filtrate. The tin and antimony are then put into sulfuric acid solution, the antimony is determined by titration with permanganate in the presence of hydrochloric acid, and the tin afterwards determined iodometrically in the same solution after reduction with test lead in an atmosphere of carbon dioxide. In the second sample, tin and antimony are filtered off, washed slightly, the filtrate is reserved, and then combined with a nitric acid solution of any contaminants recovered from the tin and antimony. Copper and lead are then determined electrolytically. Zinc is thrown out in the electrolyte as sulfide in 0.01 *N* sulfuric acid solution and ignited to oxide. Iron is then precipitated twice by ammonia and weighed as oxide. Finally nickel is thrown out and weighed as nickel dimethylglyoxime. It is thus apparent that the method calls for volumetric determinations of antimony and tin, the simultaneous electrodeposition of copper and lead, and gravimetric determinations of zinc, iron, and nickel. As is shown, the gravimetric determination of lead and volumetric determinations of zinc, iron, and nickel can be substituted without changing the main procedure.

Gravimetric methods for tin, antimony, and lead are not favored, in spite of the desirability of finally having in an analysis a compound which may be seen and tested. The gravimetric method for tin as SnO_2 is not specified on account of the impure character of the precipitate and the necessity of attempting corrections which, in the hands of novices, usually introduce greater errors than would the impurities. The volumetric method for antimony is preferred, in spite of the small amount present, on account of its rapidity and an accuracy equal to if not greater than that obtainable by ordinary care in a gravimetric determination as Sb_2O_4 or Sb_2S_3. The electrodeposition of lead is preferred in the absence of manganese and with the small amounts of lead involved, on account of the ease and rapidity of the method; there is no reason why lead cannot be separated and weighed as $PbSO_4$ prior to the electrodeposition of copper.

DETERMINATION OF ANTIMONY AND TIN

Digest 3 g. of the sample with 50 cc. of nitric acid (sp. gr. 1.2) until decomposition is complete, boil to expel oxides of nitrogen, dilute with 150 cc. of hot water, and digest for 3 or 4 hrs. on the steam bath. Filter, keeping the solution hot, through a filter of close texture, and wash a few times with hot dilute nitric acid (1 per cent by volume). Reserve the precipitate. Nearly neutralize the filtrate with ammonia, pour the solution while stirring into an excess of ammonium sulfide, and digest at the side of the steam bath for an hour. Filter, wash slightly with water containing a little ammonium sulfide, and discard the precipitate. Acidify the filtrate with hydrochloric acid added in slight excess and digest at the side of the steam bath until the sulfur and sulfides settle. Filter, wash the residue with acidulated hydrogen sulfide water, and combine the paper and its contents with the reserved precipitate.[3]

ANTIMONY—Place the papers and precipitates in a 500-cc. Erlenmeyer flask and add 25 cc. of nitric acid (sp. gr. 1.42), 5 g. of ammonium persulfate, and 15 cc. of sulfuric acid (sp. gr. 1.84). Boil until strong fumes of sulfuric acid escape. If the solution is brown, cool, and add 5 cc. of nitric acid and 1 g. of persulfate, and boil again until strong fumes appear.[4] Cool, dilute to 40 cc., add 0.5 to 1.0 g. of sodium sulfite to reduce all of the antimony to the trivalent state, and boil until sulfur dioxide is expelled. Add 200 cc. of distilled water, 20 cc. of hydrochloric acid (sp. gr. 1.19), cool to about 10° C., and titrate with a standard solution of permanganate[5] to a pink tint which persists for 10 sec. The titration should be corrected by a blank determination (usually amounting to about 0.06 to 0.08 cc. of 0.1 *N* permanganate solution) carried out on a filter paper carried through all of the steps of the determination.[6]

TIN—Pour the titrated solution into a 500-cc. Erlenmeyer flask, add 80 cc. of hydrochloric acid (sp. gr. 1.19), and insert a 3-hole stopper carrying gas inlet and outlet tubes, and having the third hole closed by a small stopper. It is advisable to use an air condenser about 15 to 20 cm. in length in the

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[3] In case the alloy does not contain much iron or antimony the above recovery may be safely omitted in routine analyses.

[4] This method of attack was used with success by the American Brass Company. At this Bureau the paper and precipitate are placed in a Kjeldahl flask, treated with 2 to 4 g. potassium sulfate and 20 cc. of sulfuric acid, and heated as in a nitrogen determination to complete solution of the sample and the destruction of organic matter.

[5] The permanganate solution should contain approximately 3.16 g. potassium permanganate per liter. The theoretical antimony titer (approximately 0.006) as calculated by standardization against oxalate may be used, although it is preferable when dealing with an alloy of high antimony content or in accurate work to standardize under like conditions against material of known antimony content.

[6] This determination is subject to interference by arsenic and vanadium. So far as is known to the authors, vanadium is not employed in this class of material. Its presence could be easily detected by a hydrogen peroxide test of the titrated solution and its interference avoided by precipitating tin and antimony by hydrogen sulfide in acid solution, filtering, and then putting the sulfides into sulfuric acid solution. As regards the interference of arsenic, its prior removal is attended by uncertainty and by danger of volatilizing tin and, particularly, antimony. Therefore with the small amounts ordinarily present (0.00 to 0.03 per cent), it is safer to titrate, calculate the apparent percentage of antimony, and then deduct 1.86 times the percentage of arsenic as separately determined. (The factor 1.86 takes into account the difference in the atomic weights of antimony and arsenic and also the excess of permanganate required to get an end-point with arsenic.) With larger amounts of arsenic a modification such as that of Stief, THIS JOURNAL, **7** (1915), 211, is called for.

gas outlet. Add 1 to 2 g. of test lead,[7] start a slow current of carbon dioxide from a Kipp generator or a cylinder, heat gradually to boiling, and boil gently for about 40 min. Finally cool in ice to about 10° C., after increasing the current of carbon dioxide in order to prevent back pressure. This may be detected by placing a bubbling tube in the gas outlet. When the solution is cold, take out the stopper in the third hole, add 5 cc. of clear starch solution from a pipet, and insert the tip of a buret containing standard iodine solution,[8] and titrate to a permanent blue tint. The titration should be corrected by a blank determination (usually amounting to 0.05 to 0.08 cc. of 0.1 *N* iodine solution) carried through the steps of the procedure.

Determination of Copper, Lead, Zinc, Iron, and Nickel

Treat 5 g. of the sample as for the determination of antimony and tin, reserve the nitric acid solution, and treat the sulfuric acid solution of tin, antimony, and impurities with 10 g. of tartaric acid, and sufficient 10 per cent potassium hydroxide solution to neutralize the acid and redissolve the precipitate formed.[9] Pass in a stream of hydrogen sulfide for 10 to 15 min., dilute to 600 to 800 cc., and digest for 2 to 3 hrs. on the steam bath, or preferably let stand over night. Filter and wash slightly with warm 1 per cent sodium or potassium sulfide solution, being careful not to allow the precipitate to run dry lest iron sulfide be oxidized and lost. Rinse as much of the sulfides as possible from the paper into the original beaker, dissolve the sulfide adhering to the paper in a small amount of hot dilute nitric acid (1:1) and boil to complete solution of the sulfides. Combine the nitric acid recovery with the reserved nitric acid filtrate and proceed as below.

COPPER AND LEAD—Neutralize the nitric acid solution with ammonia, add 1 cc. of nitric acid (sp. gr. 1.42) for every 100 cc. of solution, and electrolyze, using a platinum gauze cathode and sand-blasted gauze anode in a beaker of tall form covered with split glasses. When deposition is complete as demonstrated by the ordinary tests, the cathode and anode should be thoroughly washed with water as the beaker is lowered. Reserve the electrolyte. Dry the cathode and anode in the usual manner, weigh, and calculate copper[10] and lead.[11]

ZINC—Evaporate the electrolyte and washings to small volume, add 10 cc. of dilute sulfuric acid (1 : 1) and heat to the appearance of fumes of sulfuric acid. Cool, dilute, treat with hydrogen sulfide, filter off any precipitate, and wash with dilute sulfuric acid (1 per cent by volume) saturated with hydrogen sulfide.[12] Boil off hydrogen sulfide, add 2 drops of methyl orange solution and neutralize with ammonium hydroxide. Finally, dilute to about 100 cc. for every 0.1 g. zinc and make 0.01 *N* with sulfuric acid (1 cc. *N* acid to every 100 cc. of solution). Precipitate zinc as sulfide in cold solution, using a rapid current of hydrogen sulfide. Filter, wash with cold water, reserve the filtrate, and ignite the wet filter and contents very slowly in an oxidizing atmosphere until all carbon is destroyed. Gradually increase the temperature to 850° for complete decomposition of the zinc sulfate formed. Do not heat above 900° C. Cool and weigh as ZnO.[13]

IRON—Boil the filtrate reserved from the zinc determination until hydrogen sulfide and sulfur are expelled, using a few crystals of ammonium persulfate toward the end. Add a few drops of methyl red and then dilute ammonium hydroxide (1 : 1) drop by drop until the color of the solution changes to a distinct yellow. Boil the solution for 1 to 2 min., filter at once without washing, and reserve the filtrate. Dissolve the precipitate in a small amount of hot dilute hydrochloric acid (1 : 1), reprecipitate with ammonia as before, filter, and wash slightly with hot ammonium chloride solution (2 per cent). Add this filtrate to the one already reserved. Ignite the wet paper and precipitate in a weighed platinum crucible in an oxidizing atmosphere, treat with a drop of dilute sulfuric acid (1 : 1), 1 to 5 cc. of hydrofluoric acid, evaporate to dryness, again ignite, and weigh as Fe_2O_3.[14]

NICKEL—Acidify the combined filtrates from the iron determination, evaporate to approximately 300 cc., and filter if not absolutely clear. Nearly neutralize with ammonia, warm, add an excess of a 1 per cent alcoholic solution of dimethylglyoxime, and make slightly ammoniacal. After warm digestion for about 1 hr., filter on a weighed Gooch crucible, wash with hot water, dry at 110° to 120° for about

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[7] Some analysts prefer reduction by metallic antimony, iron, nickel, etc. The authors have found test lead to be very satisfactory, as it does not reduce in cold solution and hence does not require removal.

[8] The iodine solution is prepared by dissolving about 12.7 g. of iodine in a solution of about 20 g. of potassium iodide in a little water, diluting to one liter, and standardizing against pure tin by the method described. The starch solution is prepared by allowing raw starch to stand for 24 hrs. in very dilute hydrochloric acid, filtering, washing, and drying at 100° C. for 3 hrs. One gram of the hydrolyzed starch is then made into a paste with cold water, poured into 100 cc. of boiling water, boiled for 3 min., cooled, and allowed to settle.

[9] In case antimony is absent, sodium hydroxide may be substituted for potassium hydroxide.

[10] If the material contains much iron or antimony, or the most accurate results are desired, the copper deposit must be examined and corrected for tin and antimony as follows: Dissolve the weighed deposit in nitric acid (1 : 1), add 0.01 g. of iron as ferric nitrate, boil, and precipitate with an excess of ammonia. Filter, wash the precipitate with hot water, and dissolve it in a small amount of hot dilute hydrochloric acid (1 : 1). Pour the solution, while stirring, into a moderate excess of potassium hydroxide solution (10 per cent), pass in a rapid stream of hydrogen sulfide, and digest for a few hours on the steam bath. Filter, wash the precipitate slightly with dilute potassium sulfide solution and render the clear filtrate faintly acid with dilute hydrochloric acid. Allow the solution to stand at the side of the steam bath until the precipitate settles, filter, wash the paper and precipitate thoroughly with acidulated hydrogen sulfide water, and dissolve as much of it as possible in a little hot dilute nitric acid (1 : 1), keeping the solution. Burn the paper at the lowest possible temperature in a tared crucible, add the reserved nitric acid solution, evaporate to dryness, and ignite at a red heat in an oxidizing atmosphere. Multiply by the factor 0.788 (which serves in these small amounts for both tin and antimony) and deduct from the weight of the copper deposit.

[11] The lead deposit may be contaminated by silica, tin, and manganese. The first two are not ordinarily serious; in the case of manganese or when much lead is present, it is safer to precipitate lead as the sulfate in the combined nitric acid solutions and then proceed with the electrolysis of copper.

[12] In accurate analyses the sulfides must be ignited, copper and lead determined, and proper corrections made. In routine analyses, they would be disregarded except when appreciable in amount.

[13] Instead of the prescribed gravimetric procedure, the washed zinc sulfide may, in routine analyses, be dissolved in hydrochloric acid and titrated under the necessary definite conditions with a ferrocyanide solution which has been standardized under the same conditions against material of known zinc content.

[14] The weighed precipitate will contain all of any aluminium that may have been in the bronze. The residue may therefore be examined for aluminium by fusing it with a little sodium carbonate, dissolving the cooled melt by digestion in dilute hydrochloric acid, reducing the almost neutral solution with a few drops of ammonium bisulfite and then testing with phenylhydrazine as in the method of Hess and Campbell, as modified by E. T. Allen [*J. Am. Chem. Soc.*, **25** (1903), 421].

Instead of the prescribed procedure, the final ammonia precipitate may be dissolved, reduced, and titrated. The advantage of the gravimetric procedure lies in the opportunity afforded for investigation of the character of the ammonia precipitate.

If iron alone is to be determined in the alloy, dissolve the weighed sample in aqua regia, boil, add ammonia in excess, and filter off the iron, lead, tin, and antimony. Dissolve the precipitate in a little hot dilute sulfuric acid, filter off any lead sulfate, and treat the acid solution with hydrogen sulfide. Filter, evaporate the filtrate to copious fumes of sulfuric acid, cool, and dilute. Finally add permanganate solution to a pink tint and proceed with the reduction and titration. The above method does not provide a satisfactory separation of aluminium on account of the large excess of ammonia which is necessary in the initial treatment.

2 hrs., and weigh, as the glyoxime salt, which contains 20.31 per cent nickel.[15]

ACKNOWLEDGMENT

The authors desire to express their indebtedness to Dr. W. F. Hillebrand for his interest and aid in the work.

[15] In routine analyses the glyoxime precipitate may be filtered on paper, the wet paper wrapped in another moist "ashless" paper and then slowly and carefully ignited to NiO. It may also be dissolved in nitric acid and titrated with cyanide solution by the method of Frevert [A. A. Blair, "Chemical Analysis of Iron," 8th edition, J. B. Lippincott and Co., 182. See also G. L. Kelley and J. B. Conant, THIS JOURNAL, **8** (1916), 804].

The Analysis of Solutions of Ammonium Citrate[1,2]

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An investigation of methods of determining the ratio of ammonia to citric acid in ammonium citrate solutions points to two methods which can be relied upon to give accurate results. When properly carried out they give values which agree with each other and accurately represent the composition of the solutions analyzed.

In the formaldehyde titration method, the only precautions to be observed are that the formaldehyde shall be neutral and present in sufficient quantity to combine with all the ammonia.

In the other method the alkaline residue left after the distillation of the ammonia is made acid to methyl red with a measured amount of standard acid and titrated with standard alkali with phenolphthalein indicator.

IN the course of the study of the colorimetric method for the preparation of neutral solutions of ammonium citrate, undertaken while the senior author was associate referee on this subject for the Association of Official Agricultural Chemists, his attention was called to the diversity of procedures employed in the analysis of such solutions. As the determination of the ratio of ammonia to citric acid by analysis is one of the best ways of checking the reactions of ammonium citrate solutions the accuracy of the methods used is of considerable importance.

While referee on phosphoric acid in 1908, McCandless[4] used the determination of the ratio of ammonia to citric acid as the criterion of the reaction of solutions submitted to him. His procedure consisted of adding a measured amount of 0.25 N alkali to the citrate solution and distilling off the ammonia which was collected in a measured amount of standard acid and determined by titrating the excess acid. To the residue in the distillation flask he added "an excess" of 0.5 N acid and phenolphthalein and titrated back with 0.1 N alkali to the end-point. This procedure is apparently used in many laboratories either exactly as described by McCandless, modified as to the strength of solutions used, or by eliminating the last step and titrating the excess of the originally added standard alkali directly to a phenolphthalein end-point.

A second type of method is the so-called formaldehyde titration method suggested by Patten and Marti.[5] In this method the ammonia is removed from the sphere of action by causing it to combine with formaldehyde, as was done by Schiff.[6] The citric acid is then titrated directly to a phenolphthalein end-point.

Several collaborators claimed that they were unable to get these two types of methods to agree, and hence concluded that the second one was unreliable. Upon trying to check up the composition of some solutions by both types of methods the authors actually found that the results did not agree. However, as the formaldehyde method had been in use in this laboratory since it was first suggested and since it is in constant use in scores of other laboratories in biochemical work, the authors were skeptical as to its shortcomings. Hence the investigation of both methods was undertaken.

COMPARISON OF RESULTS

The first points studied were the agreement of these methods with each other and with themselves when used on the same solution. Needless to say, every possible precaution against error was taken. The reagents were all carefully standardized, using as a standard of reference 0.1 N HCl prepared by the method of Hulett and Bonner[7] and checked gravimetrically. The flasks and burets were all carefully calibrated. (This precaution should not be neglected. Burets have been purchased recently from reputable supply houses which upon calibration have been found to be as much as 0.4 cc. off, and variations of 0.1 cc. are common.)

The following procedures were studied:

1—The original technic of McCandless, with 0.25 N alkali for the initial stage, 0.5 N acid for the second, and 0.1 N alkali for the back titration.

2—The same technic as (1), but with 0.1 N reagents throughout.

3—The same procedure as (2), except that the addition of acid was continued until the solution was acid to methyl red.

4—Direct titration to a phenolphthalein end-point with 0.5 N HCl, after the addition of 35.00 cc. 0.5 N NaOH.

5—The formaldehyde method, with 0.1 N reagents.

The results are shown in Table I, page 430.

At the bottom of each set of determinations is shown the maximum variation among the individual estimations. It will appear at a glance that two of the methods, *viz.*, 2 and 4, give variations much larger than those in the other two methods. In calculating these variations all estimations have been considered. The proponents of these procedures will undoubtedly point out that this is unfair, since in some cases most of the figures agree fairly well, while only one or two differ materially from the rest. Thus, in the results by Method 2 on Solution II the second determination was a whole cubic centimeter lower than the next one to it. Were this result to be discarded, as, of course, it would be in practice, as being "off," the maximum variation would be reduced from 1.70 to 0.70. The same general statement applies to Determinations 4 and 5 by Method 4 on Solution II and 5 and 6 by the same method on Solution III. These results are,

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[3] Research Chemist, Michigan Agricultural College Experiment Station.

[4] *Bur. Chem., Bull.* **122**, 147; THIS JOURNAL, **6** (1914), 921.

[5] THIS JOURNAL, **5** (1913), 568.

[6] *Ann.*, **319** (1901), 76.

[7] *J. Am. Chem. Soc.*, **31** (1909), 390.

TABLE I—COMPARATIVE RESULTS WITH DIFFERENT METHODS

SOLUTION No.	DETERMINATION No.	PROCEDURE No. 1	2	3	4	5
I	1	...	26.01	26.27	...	26.09
	2	...	26.19	26.17	...	26.18
	3	...	26.32	26.22	...	26.09
	4	...	26.46	...	...	26.19
Maximum variation		...	0.45	0.10	...	0.10
AVERAGE		...	26.25	26.19	...	26.14
II	1	27.38	30.23	27.27	30.70	27.20
	2	27.46	29.23	27.48	30.05	27.24
	3	27.38	30.93	27.48	30.05	27.30
	4	27.26	30.73	27.48	31.05	27.30
	5	27.38	30.53	...	29.55	27.24
	6	...	30.38	...	30.05	27.30
Maximum variation		0.20	1.70	0.21	1.50	0.10
AVERAGE		27.37	30.34	27.38	30.24	27.25
III	1	27.40	31.02	27.08	28.46	27.03
	2	27.30	31.85	27.58	28.26	27.08
	3	27.38	32.35	27.08	28.71	27.03
	4	27.53	31.72	26.93	28.67	27.03
	5	27.55	32.25	27.29	29.36	27.08
	6	27.51	29.64	27.18	27.07	27.03
Maximum variation		0.25	2.71	0.65	2.29	0.05
AVERAGE		27.44	31.47	27.19	28.42	27.05

however, given consideration because repeated tests have shown that such discordant results continually occur and are typical of the methods. In fact, the rather close agreement of the majority of the results is to be regarded as a very insidious danger in forming a correct opinion of their value. Thus the series given, which includes three perfect checks, would indicate that with perhaps a little care in manipulation good results might be had. Only a thorough investigation of the procedures themselves and the careful repetition of many determinations have shown conclusively that consistent results cannot be obtained.

Of the five methods given, 1, 3, and 5 evidently agree much better with each other than with the other two or than the other two do with each other. (The agreement of the results on Solution I by Methods 2 and 5 as well as those on Solution II by Methods 2 and 4 are fortuitous, as will be shown later.) This was rather unexpected, since Method 1 differs from Method 2 only in the strength of the solutions employed. The explanation, however, actually does lie in the fact that in the original technic of McCandless (Method 1) a strong solution of acid was used, *i. e.*, 0.5 *N*; hence the "excess" was so large that the reaction was carried far enough to reduce the discrepancies between this method and 3 to within the limits of experimental error. In Method 2, on the other hand, the use of 0.1 *N* acid causes a smaller excess to be added beyond the phenolphthalein end-point, with the result that the figures approximate those obtained by 4 rather than by the other procedures.

The uncertain point of the whole matter is the meaning of the term "excess of acid." McCandless, of course, meant an excess over the amount of alkali not neutralized by the citric acid. He apparently assumed, and very naturally since this was the end-point ultimately sought, that this point would be shown by phenolphthalein. Unfortunately this is not the case, for on approaching it from the alkaline side a pseudo-end-point is first encountered at which the color of the indicator is discharged although some of the alkali is still unneutralized. Only when the addition of acid is continued until the reaction of the solution is below a pH of about 5.5 is all of this excess alkali neutralized. The "excess acid" can then be titrated back with alkali and a true end-point with phenolphthalein reached. The proper reaction to be passed in the addition of acid can be determined by the use of methyl red instead of phenolphthalein as the indicator. Since methyl red is pink in acid solutions and straw-colored in alkaline ones it does not interfere with the use of phenolphthalein in the same solution.

ELECTROMETRIC TITRATIONS

In order to make the relationships more clear a citrate solution was prepared and analyzed by Methods 2, 3, and 5; the courses of the titrations were followed electrometrically with a hydrogen electrode. Method 2 was repeated several times, with the addition of varying quantities of acid intermediate between those required to give solutions acid to phenolphthalein and to methyl red. For instance, 8.50 cc. 0.1 *N* HCl discharged the phenolphthalein color and 20.00 cc. produced the pink of the methyl red. Four titrations were made, with the addition of 11.00, 12.00, 14.00, and 16.00 cc. of 0.1 *N* HCl, respectively, before titrating back to the final phenolphthalein end-point. The final figures for citric acid in terms of 0.1 *N* NaOH are given in Table II and the complete titration curves are shown graphically in Fig. 1.

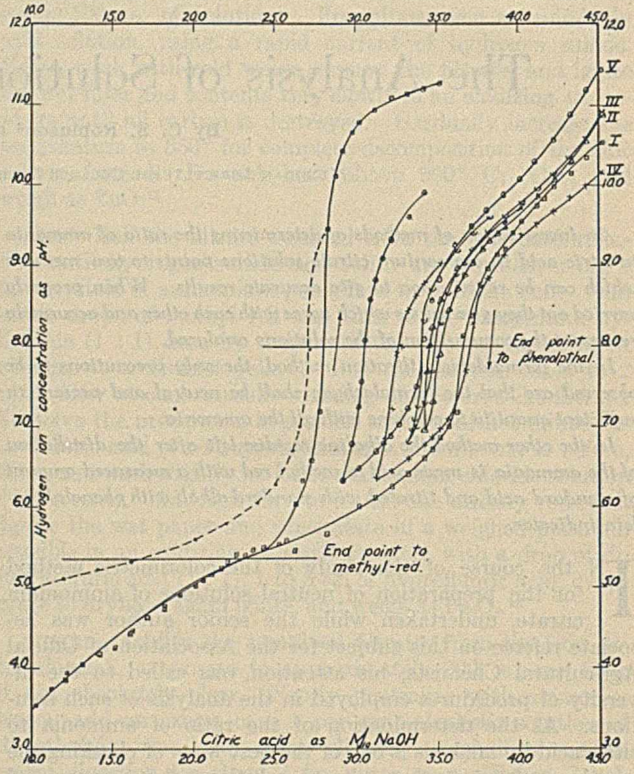

FIG. 1—ELECTROMETRIC TITRATION OF CITRATE SOLUTIONS

TABLE II—CITRIC ACID IN AMMONIUM CITRATE DETERMINED BY DIFFERENT METHODS. TITRATIONS WITH H ELECTRODE

Method 2:	CITRIC ACID
11.00 cc. 0.1 *N* HCl	34.55
12.00 cc. 0.1 *N* HCl	34.23
14.00 cc. 0.1 *N* HCl	32.55
16.00 cc. 0.1 *N* HCl	30.64
Method 3	27.77[1]
Method 5	27.20[2]

[1] Not boiled after addition of acid.

[2] Several electrometric titrations were made by Methods 3 and 5 with results agreeing as well as by the titrations with indicator. The results are omitted because of the confusion caused by a multiplicity of closely agreeing curves.

In this figure the ordinates represent pH values. The abscissae represent the cc. 0.1 *N* NaOH added less the cc. 0.1 *N* HCl added. The addition of acid is therefore shown by a decrease in the total. Except in the solutions titrated by the formaldehyde method, a total of 45.25 cc. 0.1 *N* NaOH was added to the original solution and the ammonia boiled off. This gives the starting points for all the curves on the extreme right of the figure. The addition of 0.1 *N* HCl is shown by decreasing values for the total alkali present, carrying the curves to the left with decreasing pH values. The final back titration with alkali causes the reverse to take place, *i. e.*, the curves pass upwards and to the right. The titrations were carried out with the indicators present in the solutions and the points at which the colors changed were noted.

A study of the figure shows that with the addition of acid the reaction changes rather rapidly although the curves still show a distinct change in direction coinciding with the disappearance of the phenolphthalein color. This end-point is the one used in Method 4. The poor agreement of the several curves at this point is only an exaggeration of that obtained in practice, due perhaps to the longer time required to make the separate additions of acid in the electrometric titration. Occasionally, as in the cases of Curves I and IV, perfect agreement is obtained and generally, as in the cases of Curves II, III, and V, the differences are within a range of 1 cc., but these differences are not accidental.

The situation as regards Method 2 is illustrated by the upward branches of Curves II, III, IV, and V. The end-points here follow strictly the order of the amounts of acid added, 11.00, 12.00, 14.00, and 16.00 cc. of acid used giving values for citric acid corresponding, respectively, to 34.55, 34.04, 32.55, and 30.64 cc. 0.1 *N* NaOH. Evidently the closer the amount of acid added approaches that required to give a pH of 5.5 the more closely will the results agree with those of Method 3 and the formaldehyde method. So in the case of McCandless' original technic the use of a concentrated acid caused the reaction to be carried so far that in its backward course it came very close to the true end-point.

It is to be observed that these curves differ from Curve I, in which a true excess of acid is added, in that the addition of alkali causes a sharp rise in the pH to the end-point. There is no "tail" as there is in Curve I along which the curves for the addition of acid and alkali coincide. This is but one sign of the general instability of the solutions in the range between the end-points with the two indicators. In this range there is always, on allowing the solution to stand, a "drift" in the potentiometer readings towards the alkaline side, an apparent tendency for the reaction spontaneously to get up to the reflex part of Curve I. It is this condition of unstable equilibrium which is responsible for the discordant results afforded by Methods 2 and 4 and to a lesser extent by Method 1. Even the quantity of alkali initially added has its effect, as is shown by Table III, which gives the results of analyses by Method 2, using different amounts of alkali to drive off the ammonia.

TABLE III—EFFECT OF ADDITION OF DIFFERENT AMOUNTS OF ALKALI ON CITRIC ACID VALUES BY METHOD 2

Solution	Cc. 0.1 *N* NaOH Added	Citric Acid as Cc. 0.1 *N* NaOH	Cc. 0.1 *N* NaOH Added	Citric Acid as Cc. 0.1 *N* NaOH	Cc. 0.1 *N* NaOH Added	Citric Acid as Cc. 0.1 *N* NaOH	Citric Acid by Formaldehyde Method
I	28.00	27.50	34.98	29.47	44.92	31.39	27.30
	28.00	27.50	34.98	29.77	44.92	33.49	
	28.00	27.50	34.98	29.97	44.92	32.99	
II	28.00	24.99	34.98	26.66	44.92	25.70	24.31
	28.00	24.99	34.98	27.36	44.92	25.50	
	28.00	25.10	34.98	27.76	44.92	25.80	

Other factors may, however, predominate, as in the last set of values for Solution II, which were made the day following the carrying out of the other analyses and presumably with some difference in manipulation. Only with Method 3 of this type of procedure can consistent results be had, irrespective of the above-discussed conditions. Table IV illustrates the independence of Method 3 of the amount of alkali originally added.

The question may still be raised: Do the figures obtained by these two methods actually show the composition of citrate solutions or do the true values lie in a region near the grouping of curves of Method 2 in Fig. 1? One collaborator stated that his reason for preferring Method 2 to 5 was that the former method, when used on a solution made to contain certain quantities of ammonia and citric acid, gave results agreeing more closely with the calculated values than did Method 5. This is entirely contrary to our experience. The question involved can be answered in the following manner:

TABLE IV—EFFECT OF ADDITION OF DIFFERENT AMOUNTS OF ALKALI ON CITRIC ACID VALUES BY METHOD 3

Cc. 0.1 *N* NaOH Added	Citric Acid as Cc. 0.1 *N* NaOH	Cc. 0.1 *N* NaOH Added	Citric Acid as Cc. 0.1 *N* NaOH	Cc. 0.1 *N* NaOH Added	Citric Acid as Cc. 0.1 *N* NaOH	Citric Acid by Formaldehyde Method
28.00	24.45	34.98	24.44	44.92	24.47	24.31
28.00	24.55	34.98	24.33	44.92	24.48	
28.00	24.54	34.98	24.33	44.92	24.28	
Av.	24.51		24.37		24.41	

The one solution of ammonium citrate having a known and definite ratio of citric acid to ammonia, which can be prepared without the help of any method of analysis, is a solution of the normal triammonium citrate. Such a solution can be prepared by neutralizing citric acid with ammonia by (1) the electrical conductivity method,[8] (2) the temperature method of Bell and Cowell,[9] and (3) by the electrometric titration method with a hydrogen electrode.[10]

In such a solution the ratio of ammonia to citric acid will be 1:3.759. Two such solutions were prepared using the first and third methods on each. They were analyzed by Methods 4 and 5. The results are given in Table V.

TABLE V—RESULTS OF ANALYSIS OF SOLUTIONS OF TRIAMMONIUM CITRATE BY METHODS 4 AND 5

Solution	Ratio NH_3: $C_6H_8O_7$ Method 4	Method 5
A	1 : 3.966	1 : 3.750
B	1 : 3.950	1 : 3.763

These figures are averages of six separate determinations of citric acid and ammonia by each method. Patten and Marti in their original article on the formaldehyde method likewise report the analysis of such a solution giving a ratio of 1:3.765. When it is recalled that a variation of 0.1 cc. 0.1 *N* reagent in the determination of either ammonia or citric acid makes a difference of approximately 0.015 in the ratio, the deviations of the results by Method 5 from the theoretical value are seen to be well within the limits of experimental error, and they leave no question as to which method gives the true composition of citrate solutions.

SUMMARY

Of the methods for the analysis of solutions of ammonium citrate discussed in this paper only two can be relied upon to give accurate results. When properly carried out they give values which agree with each other and which accurately represent the composition of the solutions upon which they are used.

One of these is the formaldehyde titration method. The only precautions to be observed in this method are that the formaldehyde shall be neutral and present in sufficient quantity to combine with all of the ammonia. The addition of alkali is carried to the first permanent pink of the indicator which should be present in sufficient quantity to give a distinct color.

The other procedure is carried out as follows, with solutions of the concentration ordinarily used in fertilizer analyses:

Fifty cc. of the original citrate solution are diluted to 500 cc. in a volumetric flask. Ten-cc. samples of this solution are measured in Kjeldahl flasks, an excess of standard alkali added, and the ammonia distilled off and titrated in the usual manner. The residue in the distillation flask is

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[8] *J. Am. Chem. Soc.*, **33** (1911), 711; THIS JOURNAL, **4** (1912), 443; Mich. Agr. Expt. Sta., *Tech. Bull.* **12**.

[9] *J. Am. Chem. Soc.*, **35** (1913), 49.

[10] *Ibid.*, **35** (1913), 857.

transferred to a suitable flask or beaker, some methyl red added and then standard acid until the solution is acid as shown by the appearance of the red color of the indicator. No precautions need be taken against over-running this end-point as an excess of acid is desired. The solution is then boiled to expel carbon dioxide and the excess acid titrated with standard alkali after the addition of phenolphthalein. The difference between the total alkali and acid used gives the amount of alkali neutralized by the citric acid in the sample.

Determination of Suspended Impurities in Gases[1]

By Wilfred W. Scott[2]

COLORADO SCHOOL OF MINES, GOLDEN, COLORADO

BEAM TEST

TYNDALL demonstrated that dust particles are responsible for the visibility of rays of light, such as the sunbeam or the beam of the searchlight. He did not make clear the best conditions enabling one to see the beam produced by minute amounts of suspended matter in purified gases, nor did he show that a gas free of dust may still produce a beam in presence of liquid mist. The opinion commonly current regarding the conditions necessary to see the beam produced by light rays in purified gas, is that the rays should be parallel and should be viewed with the visual axis at right angles to this beam. Observing these conditions the author failed to see the beam when using direct sunlight, but discovered that a cone of light from an arc light gave a distinct beam. This led to the discovery that the beam is best viewed by glancing towards the source of light. Accordingly the apparatus shown in Figs. 1 and 1*a* was designed.

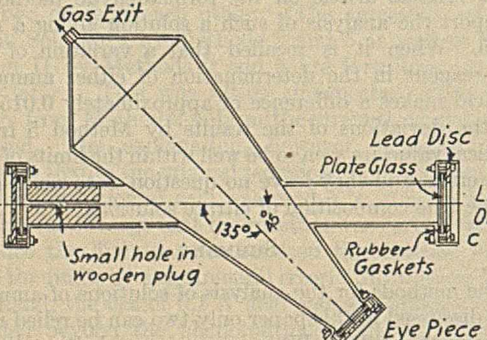

FIG. 1

For the examination of a corrosive gas, it is advisable to have the chamber of the camera made of a material not affected by that gas. For example, in examining purified contact gas a lead chamber is recommended. The interior of the chamber is blackened with dull paint that is a poor light reflector. In the apparatus shown, circular glass disks close the ends of the tubes *a*, *b*, and *c*. The gas examined enters near the eyepiece *b* and passes out at the opposite large end. The ray of light is directed through a small opening, either circular (diam.1 cm.) or a narrow slit, located at *a*, and passes through the arm of the tube and out through a glass window at *c*. The idea is to avoid light reflection in the chamber, as this would cause a glow in the tube and greatly reduce the sensibility of the test.

The beam caused by liquid mist alone appears as a uniform pencil or band of light, whereas dust particles produce a sparkling effect or irregular flashes of light. The beam is more intense with the gas in motion. Within certain limits the intensity of the beam is directly proportional to amount of suspended matter in the gas.

If the gas is dry the beam is completely removed by passing the gas through a 3-in. mat of loosely carded purified asbestos. If the gas, thus purified of solid matter, is passed through a liquid the beam again becomes apparent. From this it is evident that the test must be applied to dry gas if it is desired to ascertain the presence of solid matter in suspension.

Fig. 2 shows the apparatus set up for ascertaining the effectiveness of a scrubber in a quantitative determination of the solid and liquid suspended matter in a gas. The apparatus is so arranged that comparisons may be made of the unfiltered gas, by means of a bypass with that of the filtered or purified gas. Advantage is taken of the difference in pressures at A and B, so that a continuous sample may be taken of the gas without the necessity of an aspirator. A hand arc light shown on the left furnishes the rays of light which enter at *a* and pass out into the air at *c*. The beam is viewed through the eyepiece *b*. The meter measures the volume of gas aspirated.

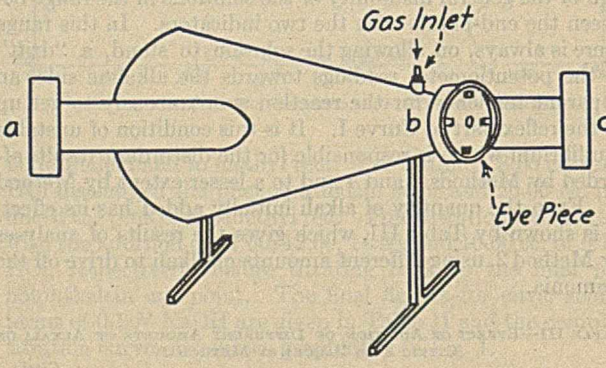

FIG. 1*a*

DETERMINATION OF SOLID AND LIQUID IMPURITIES

Solid or liquid impurities suspended in a gas may be removed quantitatively by passing the gas through a filter of loosely carded dry asbestos. A filter 2 in. thick and 1.25 in. in diameter is effective in removing suspended matter completely with gas passing through it at the rate of 2 to 3 l. per sec. (5 to 7 cu. ft. per min.). It is essential that the asbestos be free from condensed moisture as a soggy filter is not effective for gas filtration.

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[1] Received March 3, 1922. Published by courtesy of D. Van Nostrand Co., New York, N. Y.

[2] Associate Professor of Chemistry, Colorado School of Mines; Editor of "Standard Methods of Chemical Analysis."

DETERMINATION OF SULFURIC ACID MIST IN GAS—The gas is aspirated through a filter of well-carded, blue fiber, purified asbestos, the asbestos extracted with water and the extract titrated with standard alkali.

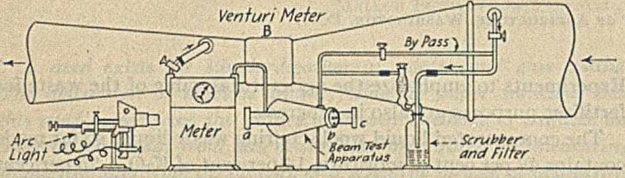

FIG. 2

APPARATUS—An ordinary 1.25-in. filter tube funnel (see Fig. 3) with long stem, to permit a sample being drawn directly from the flue, may be used. If the gas is supersaturated with moisture it is advisable to use the form of apparatus shown in Fig. 4, the bottle serving as a condensing chamber to avoid water condensation on the asbestos. Occasionally it is necessary to pass the gas through two such chambers to remove the condensed moisture from warm moist gases.

The funnel is packed first with a layer of glass wool, followed by a two-inch layer of well-carded, purified, blue asbestos, and finally a second layer of glass wool. The glass wool prevents the asbestos plugging the inlet and exit openings. Perforated disks may be used in place of the glass wool.

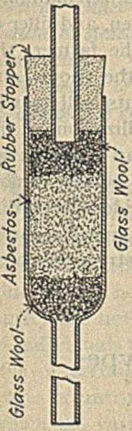

FIG. 3

The asbestos is the blue African form. White asbestos will not give accurate results, as this is attacked slightly by dilute sulfuric acid and decidedly so by strong sulfuric. The blue form is not appreciably attacked, so that the acid may be extracted as free acid by water. The asbestos is purified by digesting with nitric acid, followed by a second digestion with hydrochloric acid. The material is now thoroughly washed to remove the acids and is dried. The dry asbestos is placed in wide-mouthed bottles until required. Before using it is carded or fluffed out by means of a pick and then placed loosely in the funnel to be used in the test.

Asbestos	SiO_2	CaO	MgO	FeO	Al_2O_3	MnO	H_2O
Blue African	49.0	1.2	2.7	24.4	11.9	..	..
White Canadian	40.3	..	43.4	0.9	2.3	..	13.7
White Italian	55.9	17.8	20.3	..	4.3	1.1	..

THE TEST—The gas is aspirated through the filter at the rate of about 5 cu. ft. per min., the gas being measured by a dry gas meter following the apparatus. When a volume of 10 to 100 cu. ft. of gas has been aspirated, the amount depending upon the amount of acid mist present in the gas, the asbestos filter is placed in a beaker. (If SO_2 is present in the gas, as is the case in contact sulfur gases, air is first passed through the asbestos to remove the SO_2.) The tube is rinsed out, and the rinsings poured on the asbestos. The contents of the the beaker are now transferred to a 2-in. Büchner funnel in position on a half-liter capacity suction bottle. The water is drawn out of the asbestos and the filtrate passed through the mat, thus formed, to remove the asbestos fibers. The mat is washed with small portions of pure water until free of acid, and the extract, transferred to a beaker, is titrated with standard alkali (0.05 *N* has been found to be satisfactory). Methyl orange is used as an indicator.

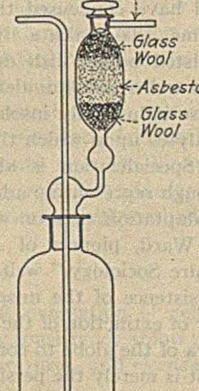

FIG. 4

DETERMINATION OF ARSENIC IN GAS—The test is the same as the one described for determining sulfuric acid. An aliquot portion of the water extract is taken for a Gutzeit determination of arsenic. Arsenic in purified contact gas is carried in the acid mist.

DETERMINATION OF CHLORIDES—A portion of the water extract, obtained by the procedure described under the test for acid in gas and filtered through paper if necessary, is examined for chloride by the turbidity test by addition of nitric acid followed by silver nitrate reagent. Comparison is made with a standard using either Nessler tubes or a colorimeter. If the amount of chloride is too great for a turbidity test a gravimetric determination should be made, or the aliquot portion taken should be sufficiently diluted with water to enable the turbidity test to be made. The standard should contain the same amount of sulfuric acid as the sample. The extract should be free of asbestos fiber.

Liquid Oxygen Explosives

Although the use of liquid oxygen explosives has not yet made much headway in the United States, experiments made with such explosives by a metal-mining company at Pachuca, Mexico, operated by American capital promise quite satisfactory results, according to observations made by a representative of the United States Bureau of Mines. From the beginning of the entrance of the United States into the World War, efforts have been made by George S. Rice, Chief Mining Engineer of the Bureau of Mines, to have liquid oxygen explosives tried out practically in this country. Owing to the fact, however, that no manufacturer in the United States makes oxygen liquefying plants, the use of these explosives in America has been quite limited. The development of this innovation so far has been largely German, and in Germany oxygen liquefying plants are manufactured in various sizes in complete units of apparatus and containers.

Since the war the only extensive development outside of Germany has been in the Lorraine iron mines where the Germans installed apparatus, and additional apparatus has been put in by the French. One company in Lorraine is mining its entire annual output of 1,500,000 tons of iron ore by the use of these explosives. This company has developed a cartridge of its own on which it has received patents, and has applied for others. It is claimed that the cartridge is an improvement on the German cartridge. The Germans use for brisant effects, soot; and for slow heaving effects, wood pulp. Either fuse or electric detonators can be used for igniting the charge. The Germans have now developed a method of placing the electric detonator in the bottom of the hole in a special container and have been able to fire large rounds, it is claimed as high as twenty-eight shots at a time.

Fastness of Dyes

The National Council of Dyes and Colors held a meeting in New York City on March 20 and elected Mr. David N. Mosessohn of the Associated Dress Industries of America, permanent chairman. The secretary, Dr. J. Merritt Matthews, proposed that something of a definite and concrete nature should be undertaken by the Council and proposed that each of the industries interested and associated with the Council should definitely formulate the various staple fabrics in which they are particularly interested and state what qualities of colors with respect to fastness or other properties should normally be expected on these fabrics, so that data would be available regarding the commercial requirements for colors on fabrics. As a result, a motion was passed instructing the secretary to write to the representatives of the various industries to secure definite data as to the qualities of fastness required on the different staple fabrics and to present a report at the next meeting of the Council if possible. It was also voted to distribute 4000 reprints of Mr. Haynes' report on certain tests made on colored fabrics.

Wool Scouring Wastes for Fertilizer Purposes[1]

By F. P. Veitch[2]

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THIS country uses more than 600,000,000 lbs. of unscoured wool annually. Approximately half this weight consists of dirt, salts, grease, and albuminous and other organic matter which must be removed by careful washing. With the exception of the grease recovered at a few of the scouring plants, all of this material is wasted, being run into the streams of the country, seriously polluting the waters and rendering them unfit for domestic and many industrial purposes without purification at great expense.

Analyses of a large number of samples of all grades of unscoured wool, both domestic and foreign, show that the grease content varies from 6 to 42 per cent, averaging 14 per cent; that the water-soluble matter varies from 6 to 33 per cent, averaging 14 per cent; that the nitrogen (other than that of the wool) varies from 0.3 to 1.1 per cent, averaging 0.6 per cent; and that the potash varies from 1 to 7 per cent, averaging 4 per cent.

Both the potash and the nitrogen compounds are water-soluble, and it is these and the other water-soluble constituents of wool that are of interest as fertilizer materials.

Under present conditions, the wool scouring plants of this country are wasting annually potash equivalent to approximately 100,000 tons of Kainit, worth at present quotations $840,000, and 42,000 tons of 4.5 per cent tankage, worth $280,000 to the fertilizer manufacturer.

A number of attempts have been made both in this country and abroad to recover potash salts and other valuable constituents from wool scouring waste, but apparently without success, except for the relatively small proportion of grease that is being recovered by the centrifugal, cracking, and extraction processes. The problem should not be regarded as hopeless, however. It is believed that wool scouring wastes can be utilized at a profit, and that before long some procedure other than running them into the water courses of the country must be developed. In fact, some of the states are now very active in protecting water courses against pollution by trade wastes, especially against wool scouring wastes, which are among the most offensive and injurious. Wool scouring plants must purify their waste wash water at great expense and with little, if any, compensation from the sale of recovered products.

It is with the hope of working out economical processes for the recovery and utilization of all the useful constituents of wool scouring wastes that these investigations were begun by the Bureau of Chemistry. The cordial coöperation of the wool scouring industry on the one hand and of the fertilizer manufacturer on the other, without which the work cannot be carried to a successful conclusion, is sought.

Experiments have been conducted on a manufacturing scale in mixing concentrated wool scouring wastes with other waste materials for the purpose of determining the practicability of economically handling the material in the fertilizer factory. The material gave no trouble and the fertilizer manufacturer is ready to use the material as soon as it can be obtained in quantity, and, of course, at a price that will yield him a profit. "Base goods" have also been prepared on a factory scale, using the concentrated wool scouring liquors as the source of part of the potash and nitrogen. These experiments have also shown clearly that there is no difficulty in working the liquors in making base goods. Experiments to emphasize the agricultural value of the waste for fertilizer purposes are also in progress.

The concentrated liquid wool scouring waste liquor so far made contains 42 per cent of moisture, 14 per cent of K_2O, 1.25 per cent of nitrogen, and 14 per cent of grease, while the dried and degreased waste contains 24.5 per cent K_2O, 25.5 per cent nitrogen, and 0.6 per cent of grease. Fertilizer material made from the concentrated waste and another waste material on a factory scale contains 6.5 per cent water-soluble K_2O, 6.1 per cent total nitrogen, 3.4 per cent water-soluble nitrogen, 1.9 per cent alkaline permanganate-, and 1 per cent neutral permanganate-insoluble nitrogen, and 6.8 per cent of grease. This material is in excellent mechanical condition, may be handled easily in fertilizer mixing and grinding machinery, and in addition is a good dryer, with a dark color and a fine strong odor.

The work that has so far been done strongly indicates that wool scouring waste can be readily handled by the fertilizer manufacturer, giving him another source of potash, nitrogen, and filler of excellent quality, in an advantageous form. The farmer, the fertilizer manufacturer, the wool scourer, and the people and industries in the vicinity of wool scouring plants will benefit directly or indirectly from the recovery and utilization of the valuable but offensive and dangerous waste if it can be recovered economically. This, one of the most important points, is now being investigated with every hope of success, provided the cordial coöperation of the wool scourers and the fertilizer manufacturers can be had. So far the response of these industries has been most gratifying.

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[1] Presented before the Division of Fertilizer Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] Chemist in Charge, Leather and Paper Laboratory.

Reversion to Generalized Types

By H. W. Jordan

133 Stolp Ave., Syracuse, New York

Throughout industrial America hundreds of graduate chemists and engineers, ousted from their modern, specialized industries by economic readjustment, following victory in the chemists' world war, have reverted to ancient, generalized commerce.

Some who were fortunate enough to own their homes are piecing out meager commercial incomes by discharging the servant and renting spare rooms. Others have sold their homes and have condensed their families within two boarding-house rooms. To make a living they are selling life insurance and unlisted bonds; dish drainers and sewing machines; ice cream pies and near-silk underwear. In plodding from house to house, these industrially insoluble scientists are making a lot of social analyses upon which they will report in due season.

"Specialization is always preparation for destruction. Although representing adaptation to existing conditions, it becomes inadaptation so soon as those conditions change," said Lester F. Ward, pioneer of American sociology in his classic work, "Pure Sociology," written twenty years ago. "The law of the persistence of the unspecialized is only the counterpart of the law of extinction of the specialized. What we have in the living flora of the globe to compare with those great fallen races of the past is merely the persisting, unspecialized types which escaped destruction simply because unspecialized," he adds.

Unless we chemists and engineers broaden our field of remunerative work by research and practical scientific activity in cultivation of social, economic fields, it is back to the dish drainers and sewing machines for us.

The Evaluation of Gelatin and Glue[1]

By Robert Herman Bogue[2]

MELLON INSTITUTE OF INDUSTRIAL RESEARCH, PITTSBURGH, PENNSYLVANIA

A need exists for standardization in gelatin and glue testing. The discussion of methods in the following paper indicates that this need arises from the failure of present methods to evaluate the material correctly, from lack of standard procedures for measuring properties, and from the absence of a scientific method of expressing the data which are obtained.

The gelatin content of glue or gelatin, and also the joint strength of a glue, may be correctly indicated by a melting point determination; neither may be assumed to be, in all cases, proportional to jelly consistency or to viscosity at 60° C. The measurement of the viscosity of an 18 per cent solution (dry basis) at 35° C. by means of the MacMichael viscosimeter has been shown to be especially well adapted as an indirect estimation of the differentiation of glues and gelatins in the order of their melting points, and is recommended as the basis for the primary evaluation of these products. Tests of jelly consistency and viscosity at 60° C. are of value in secondary evaluation, in determining the adaptability of a given glue to a given service. Other special tests are of course of value, but methods should be stated and a uniform method of expressing results should be adopted.

A system of designating the grade of a product, based on the results of this viscosity, is outlined in the paper.

VERY few substances which are extensively employed in the trades and the arts offer so much embarrassment to either the layman or the chemist in defining, or specifying, or testing their quality or purity as do gelatin and glue. Many factors contribute to this situation. Commercial gelatin and glue are by no means definite substances, and simple tests for purity are not available. Tests which are believed by one set of individuals or manufacturers to be comprehensive and indicative of certain fundamental properties are regarded as inadequate or untrustworthy by another set. Moreover the uses for which the various gelatins and glues are employed are so divergent that tests or analyses which may be entirely adequate for some given service would be quite useless as an indication of the value of the material for some other service.

The United States Bureau of Chemistry[1]* in 1910 accepted Fernbach's[2] statement that chemical analysis gives little information in regard to the value of a glue except in a few isolated and unimportant instances. The tests described by the Bureau of Chemistry *Bulletin* are moisture, ash, reaction, gelatin (nitrogen × 5.56), water absorption, viscosity (Engler), jelly strength (Lipowitz method), and melting point (by Cambon's fusiometer). Several of these tests are certainly obsolete. Nitrogen times a factor means nothing and is misleading, unless the sample be pure unhydrolyzed gelatin, which is almost never the case. Water absorption varies with too many incidental factors, and has little significance. The Engler viscosity test, the Lipowitz jelly strength test, and the Cambon melting point test have largely been replaced in most laboratories by more recent methods or apparatus.

PRESENT METHODS

The procedures in current use for the evaluation of gelatin and glue are based *primarily* upon the jelly consistency at low temperatures or the viscosity at high temperatures, and *secondarily* upon other incidental characteristics which depend upon the service for which they are designed. The Peter Cooper system of grading may be taken as typical of American practice. Because this system was the earliest recognized attempt at glue grading in this country, and has been in continuous service since its inception in 1844, it is recognized as a kind of American standard to which other glues produced by other houses may be referred in terms that will be at least partly intelligible to the professional glue buyer. The various manufacturing houses use symbols, however, expressive of their several grades, which are more or less zealously guarded as a kind of relic of alchemic mystery, but the consumer is enlightened upon their meaning only to the extent of learning that the glue in question is equivalent in jelly strength, for example, to the Peter Cooper grade 1$^{3}/_{8}$, or equivalent in viscosity to the Peter Cooper grade 1$^{1}/_{4}$. Thus the Peter Cooper system may be looked upon as a standard for reference.

Alexander[3] has proposed the substitution of figures varying by ten points each for the symbols of Peter Cooper, and has defined the jelly strength in ounces and in grams at 10° C. (measured by his jelly strength tester) to which the numbers correspond. The viscosity test (as measured by his instrument) is also used by him.

Table I expresses this system of grading:

TABLE I—ALEXANDER'S GLUE STANDARDS

STANDARD	Peter Cooper Grade	Viscosity 80° C.	Allowable Variation in Viscosity	JELLY STRENGTH In Oz. 10° C.	JELLY STRENGTH In G. 10° C.
10	...	15.5	± 0.25	...	....
20	...	16	± 0.25	...	....
30	2	16.5	± 0.25	...	....
40	1$^{7}/_{8}$	17	± 0.25	60	1701
50	1$^{3}/_{4}$	18	± 0.5	82	2324
60	1$^{5}/_{8}$	19	± 0.5	104	2948
70	1$^{1}/_{2}$	20	± 0.5	126	3572
80	1$^{3}/_{8}$	21	± 0.5	148	4196
90	1$^{1}/_{4}$	22	± 0.75	170	4820
100	1 X	23	± 0.75	192	5443
110	1	24	± 0.75	214	6067
120	1 extra	25	± 1	236	6691
130	A extra	26	± 3	258	7314
140	...	28	± 5	...	....
150	...	34	± 8	...	....
160	...	40	±12	...	....

Kahrs[4] in 1898 proposed a rather radical departure from the then existing (and still existing) disposition on the part of glue manufacturers to grade their product by tests which were intelligible and valuable to the buyer. He urged the adoption of four tests, *i. e.*, adhesion, economic value, cohesion, and congealing point. By *adhesion* he meant the viscosity, which was expressed in terms of the weight of dry glue necessary to make up 100 unit weights of the liquid material of the proper viscosity for application in joint work. This figure Kahrs found to vary from 29 to 60. That is, in the highest grade of glue a 29 per cent solution, and in the lowest grade a 60 per cent solution, was required to give a liquid of the correct consistency at about 60° C. for service in joining work.

The *economic value* was obtained by multiplying the adhesion value by the price per pound of the glue in question, and represented therefore the price of 100 lbs. of the liquid glue ready for application. Thus at 18 cents for the highest and 5.5 cents for the lowest grades (Kahrs' figures) the cost per 100 pounds of the liquid glue would be 18 × 29 = \$5.22 for the highest grade and 5.5 × 60 = \$3.30 for the lowest grade.

The *cohesion or strength* was measured by the crushing strength of the glue jelly made up at the concentration found under adhesion, and at a temperature of 65° F. (about 18° C.). The high

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[1] Read at the Symposium on Gelatin and Glue before the New York Section of the American Chemical Society, New York, N. Y., January 6, 1922.

[2] Industrial Fellow of the Mellon Institute of Industrial Research of Pittsburgh, and Research Chemist for Armour and Co., of Chicago.

* Numbers in the text refer to Bibliography at end of paper.

temperature was used as it more nearly approached the temperature at which the glued joints would be used. This test was later substituted in part by an actual joint strength test.

The *congealing point* was measured as the temperature at which the glue, made up in the concentration indicated by the adhesion test, congealed to a jelly. This was found to vary from 91° to 75° F. and the interval of 16° was divided into ten "setting grades."

The test of the glue was then expressed somewhat as shown in Table II.

Table II—Kahrs' Glue Tests

Number	Price per Lb., Cents	Adhesion (Wt. per 100 Lbs. Standard Liquid)	Economic Value (Price per 100 Lbs. Liquid)	Cohesion (Strength)	Congealing Point
2942	18	29.3	$5.27	25	91.7
2924	5.5	57.8	$3.18	15	77.5

There are many interesting points in such a system. The table will show that although the first glue costs more than three times as much as the second, per pound, yet per unit volume of liquid ready to use it costs only six-tenths more. But it is shown to be worth more in producing, at that dilution, a greater strength, and in setting at a higher temperature, *i. e.*, more rapidly at any given temperature. Such a system enables one to see at a glance exactly wherein the differences in the glues lie, and to form an intelligent basis for judging between them. It at least gets down to salient and understandable data, which is much more than can be said for some systems now in use.

Thiele[5] bases the commercial value of edible gelatin on its viscosity (Engler), melting point, and color value.

PRIMARY AND SECONDARY TESTS—There is a difference of opinion as to what test should be regarded as the most *fundamental.* In Germany the viscosity test proposed by Fels,[6] made by the use of the Engler viscosimeter at 35° C., seems to be in greatest favor. In Italy a combination of viscosity and melting point is used.[7] In France and England the viscosity test and the melting point test by Cambon's fusiometer are employed. In this country the jelly consistency or strength is probably more used than any other test, although the viscosity test is in favor in many houses, and the melting point test by various methods is used. The quality of the material and the price are primarily rated upon these tests—sometimes a single one, and sometimes a combination of two or more. Clayton[8] concludes that the "observations seem to show that while it would be rash to form a judgment on glue from a single test, the evidences afforded by a number may be irresistible. The expert's surest system appears to be, not to rely on single short-cut tests of general quality, but to employ a number of methods including any having special bearing on the prospective or present uses of the glue, and then to base his conclusions on a consideration of all the results together." And Alexander[3] who cites the above, adds, "The truth of the matter is that the figures have a partial value, and then only to a glue expert." That is precisely the situation that the chemist should set himself to eradicate. Figures which mean little or nothing should be substituted if possible by data which do mean something, and which persons other than glue experts may comprehend.

The *secondary* basis for glue or gelatin evaluation lies in many or few other tests which are employed to determine the *applicability* of the material for any special service. For example, where the glue is to be used in mechanical spreaders, the tendency to foam is undesirable, and the foam test is of value. If the glue is to be applied by hand, the foam test is of little or no significance. If the glue is for use on paper as a size or on wall paper as a binder for the clay filler, grease should not be present in large amount, because it would form little droplets, making elliptical "eyes" or spots on the paper. In admixture with certain dyes the presence of acid or alkali is not permissible as the dye would be affected in one way or another. Suitable tests must accordingly be made upon glues designed for such purposes. Gelatin for use in photographic films or in printing rollers must have high jelly strength; if used for food or medicinal purposes it must be free from harmful impurities; if used in making marshmallows or other emulsions, a high viscosity and foam are desirable. Such a list could be greatly extended, and the *adaptability* of any glue or gelatin for its several uses is largely determined by such *secondary* tests.

The influence which such properties should exert upon the selling price of the product should be proportional, however, only to the extra cost involved in manufacturing any specialized type of material, and on the laws of supply and demand. If an extra clear glue is required the consumer should be properly expected to pay for the extra cost of clarification and filtration, and such extra cost should properly be figured on a sliding scale, dependent upon the final color and clarity, to be added to the cost of the untreated glue of the corresponding grade. For the textile trades where precipitation with alum must not occur; for veneer glues where foam is very objectionable; and for all other trades requiring glues of specific properties, the price should similarly be based upon a sliding scale to be applied to the market price of the regular corresponding grade. Where no extra cost is involved in the production of a specified glue, the sliding scale may apply according to the usual dictum supply and demand, but *it would seem most expeditious to base all such variations upon a standard primary evaluation.*

Diversity of Current Tests

The very large number of tests that have been used or proposed for carrying out the desired or required measurements makes it impossible at this time properly to discuss each and bring out the several merits and disadvantages attendant upon their use. In order, however, that some conception may be had of the extent and diversity of the proposed methods, a brief compendium may not be out of place.

For the measurement of jelly consistency, the finger test,[9] made by pressing the fingers on the jelly and comparing the firmness with that of a standard jelly under identical conditions, is still highly regarded by some testers. Of the early instruments proposed, the one designed by Lipowitz[10] in 1861 is still much used. The test consists in adding shot to a funnel, placed over a piston resting on a jelly, until the piston is forced nearly to the bottom of the glass, and the result expressed in terms of the weight of shot plus the weight of the apparatus. Kissling[11] noted the time taken by rods of different metals to sink through the jelly. Valenta[12] used a modified form of the Lipowitz instrument. Scott[13] forced a rod, terminating in a conical metallic head, into a jelly placed on a spring balance, and measured the deflection of the pointer at the moment the surface of the jelly was broken. Alexander[3] forced a cylindrical brass cup down upon a block of jelly, in the form of a truncated cone which had been removed from its container, by the addition of lead shot to the cup, until a certain outward expansion was reached, which point was indicated by the closing of an electric circuit causing a bell to ring. The weight of the shot and cup indicated the strength of the jelly. Sindall and Bacon[14] poured mercury into a glass bulb, placed upon the abraded surface of a jelly, until the bulb was forced to a half inch from the bottom, and then weighed the mercury. The Forest Products Laboratory[15] at Madison, Wisconsin, has adopted an instrument by which a weighted conical brass head is allowed to rest upon a jelly. By means of scale marked upon a frame in which the plunger slides, the depression of the plunger may be read off in millimeters. E. S. Smith[16] measured the hydrostatic pressure necessary to force a rubber diaphragm downward into a jelly a specified amount. Hulbert[17] has suggested a modification of this instrument. Low[18] has reported very satisfactory results from the use of Smith's original instrument, and regards it as more suitable for general glue work than the modification of Hulbert. C. R. Smith[19] causes a truncated cone of jelly to solidify in a funnel and then applies reduced pressure to the under surface and measures the depression of the upper surface. Sheppard and his collaborators[20] have developed an instrument by which the torsional stress of a cylinder of jelly is obtained, as well as the actual breaking load. He employs the formula

$$\frac{\text{Breaking load} \times \text{per cent twist}}{\text{Cross-section area}}$$

as the true measure of the jelly strength. This is the only truly scientific method that has yet been proposed. Oakes[21] has described the Schweizer jelly testing apparatus, which consists of a balance, in one pan of which is placed an empty beaker, and to the bottom of which is soldered a blunt plunger. These are counterpoised so that the pointers rest at zero. The jelly in a tumbler is brought into contact with the plunger, and water is allowed to run into the beaker until the pointer has reached an arbitrarily fixed deflection.

In viscosity measurements the situation is about the same. The Saybolt, Engler, and Redwood instruments have all been used. Pipet types of various designs have been described[22] and one or another of these seems in general to be most widely used. Cope[23] applied a centrifugal force to the liquid while emerging through a capillary. C. R. Smith[24] and Faust[25] have applied the "bubble method" by noting the time taken for a bubble of air of standard size to rise a given distance through the liquid. Stokes' falling sphere method has been applied recently by Sheppard,[26] Gibson and Jacobs,[27] and Fischer.[28] Flowers[29] has added the rolling sphere method to the list. Doolittle[30] described an instrument of the torsional type, an oscillating cylinder being suspended in the liquid. Garrett[31] has used a very similar device. The Couette instrument,[32] somewhat similar except that the cup containing the liquid is very slowly rotated, has been used by Hatschek[33] for exact studies on the viscosity of emulsoids. The Stormer viscosimeter has been employed by Rogers and Sabin,[34] Rigg and Carpenter,[35] and Higgins and Pitman.[36] The MacMichael instrument, described by MacMichael,[37] Herschel,[38] and Hayes and Lewis,[39] has been employed with success upon animal glues by Bogue[40] and upon casein glues by Zoller.[41]

Many methods have likewise been suggested for the melting-point determination. Chercheffski[42] measured the temperature at which small cubes of jelly became soft enough to lose their cohesion. Kissling[43] noted the temperature at which the surface of a jelly in a test tube placed horizontally became inclined. Winkelblech[44] shook a glue solution in cold water until the material had reached a consistency such that the thermometer placed vertically therein remained stationary. Küttner and Ulrich[45] describe the use of Cambon's fusiometer which consists of a metallic bowl of given dimensions and weight. A glue is allowed to gel therein, a rod being held in a vertical position in the solution. The whole is then placed in a beaker of warm water, suspended by the rod, and the temperature at which the bowl drops from the rod taken as the melting point. Herold[46] allowed a thermometer to become congealed in a test tube of glue, and noted the temperature at which the tube fell away from the thermometer when suspended in water. Sammett[47] noted the order of melting of various samples of glue when the water-swollen granules were placed on an inclined copper strip dipping in warm water. Clark and DuBois[48] determined the minimum concentration of a gelatin which would remain firm when, after making into a jelly below 10° C., the material was brought up to the temperature of 10°. C. R. Smith[49] determined the temperature at which a gelatin solution maintained a stipulated degree of viscosity, as obtained by the "bubble" method. Bogue[40] has found the viscosity at 32° to 35° C. to differentiate glues correctly according to their melting points. Sheppard and Sweet[50] have determined the temperature at which bubbles of air under a definite low pressure cease to flow through a gelatin sol.

Many other kinds of tests have also been suggested. The adhesive strength test has been used by Khars,[51] Gill,[52] Rudeloff,[53] the Forest Products Laboratory,[54] and others.[55] The tensile strength has been employed by Setherberg,[56] Gill,[52] and Hopp.[57] Optical rotation has been applied to glue testing by C. R. Smith.[19] The swelling capacity and rate of setting are occasionally mentioned as criteria for glue value.[58]

Several proposals have likewise been made for evaluating glues and gelatins by chemical means. Stelling[59] precipitates the gelatin with alcohol and determines the percentage of "non-glues" by evaporating aliquot portions of the filtrate. Precipitation of the gelatin by tannin has been used by a number of early investigators. Jean[60] used an excess of tannin and determined the excess with iodine. The value of his glues was then proportional to the amount of tannin required for precipitation. Modifications of this procedure were used by Gantter,[61] Müller,[62] Halla,[63] and Trunkel.[64] The picric acid precipitation was applied by Berrar.[65] Fahrion[66] estimated the water ash, unsaponifiable matter, fatty acids, and oxyacids, and by subtraction from 100 obtained "proteid substance." Mavrojannis[67] proposed the use of formaldehyde to separate protein and proteose from the more completely hydrolyzed peptones and amino acids. Greifenhagen, König, and Scholl[68] recommend the use of mercuric chloride and zinc sulfate. The former they claim throws down only proteoses, while the latter precipitates both protein and proteose. By difference the protein is calculated. Trotman and Hackford[69] separated the "albumoses," which included both protein and proteose, by saturating the solution with zinc sulfate. Bogue[70] has thrown down the protein with half-saturated magnesium sulfate and the protein and proteose together with the saturated salt.

This description of methods is sufficiently comprehensive to enable one to appreciate more clearly just what is signified by the statement that there is no standard procedure for the testing of glues and gelatins. In the absence of such a standard method, the diversity of tests used, as shown above, makes hopeless any attempt at an intelligent understanding of the complete significance of glue grades.

THE SCIENTIFIC BASIS OF EVALUATION

Recent researches upon gelatin have brought to light many relationships that should be incorporated into the scheme of primary evaluation. From the point of view of the chemist, gelatin is a chemical compound, a pure protein, and glue is a mixture of gelatin with the products of gelatin hydrolysis, sometimes referred to as β-gelatin, and other impurities in varying amounts. Commercial gelatin and glue should, therefore, from the standpoint of *chemical constitution* be primarily evaluated in terms of the proportion of pure unhydrolyzed gelatin which is contained in the material. From the point of view of the major glue trade, *i. e.*, the use of glue as an *adhesive*, glue should be evaluated in terms of the strength of the joint, produced under the most favorable conditions, which may be made with the material. Fortunately these two points of view—that of the chemist and that of the joiner—have been shown to be identical. The glue with the largest amount of unhydrolyzed gelatin produces the strongest joint.[70]

In the primary evaluation of the material, therefore, one or the other of these two properties should be measured, or else some variable which has been found by repeated and exhaustive tests to be directly dependent upon these properties, and to express them correctly. The direct determination of either the gelatin content or the joint strength is difficult and impracticable for routine control. So the alternative procedure must be adopted. Extensive tests have been made in the author's[70] laboratory upon the relations which the jelly strength, the viscosity, and the melting point bear both to gelatin content and to joint strength, and the data obtained show clearly that if the viscosity be held constant the gelatin content and joint strength will vary as the jelly consistency, while if the latter be held constant these properties will vary as the viscosity. But the jelly consistency and the viscosity are also shown to bear the same relation to the melting point, while the latter appears to define with precision the gelatin content and the joint strength. Any method, therefore, which accurately estimates the melting point or differentiates the glues in the same order as would result from the melting point test should be a satisfactory basis for evaluation. In most glues and gelatins the viscosity and the jelly consistency are perfectly parallel functions, and a given jelly consistency will imply a definite viscosity, or vice versa, but there are many exceptions to this generality—so many in fact that were we to use either the jelly consistency or the viscosity alone as a basis of evaluation, a large number of glues would be incorrectly graded. For example, a given glue of $1^1/_4$ grade (Peter Cooper) and 22 viscosity (Alexander) may show a joining strength of, say, 2000 lbs. per sq. in. The same grade with a viscosity of 23 may show perhaps 2200 lbs. Or a grade of $1^3/_8$ and a viscosity of 22 may show 1800 lbs. Obviously, if evaluation were correctly based upon jelly consistency, the first two examples should show the same strength, and if based upon viscosity (at 60° to 80° C.), the first and third examples should be identical.

The melting point appears to be controlled by both the jelly consistency and the viscosity, and would therefore, in the cases cited, be highest in the second, intermediate in the first, and lowest in the third, which is also the order of the strength. The melting point test seems in fact to be the most readily available and practicable test as the basis for glue and gelatin evaluation.

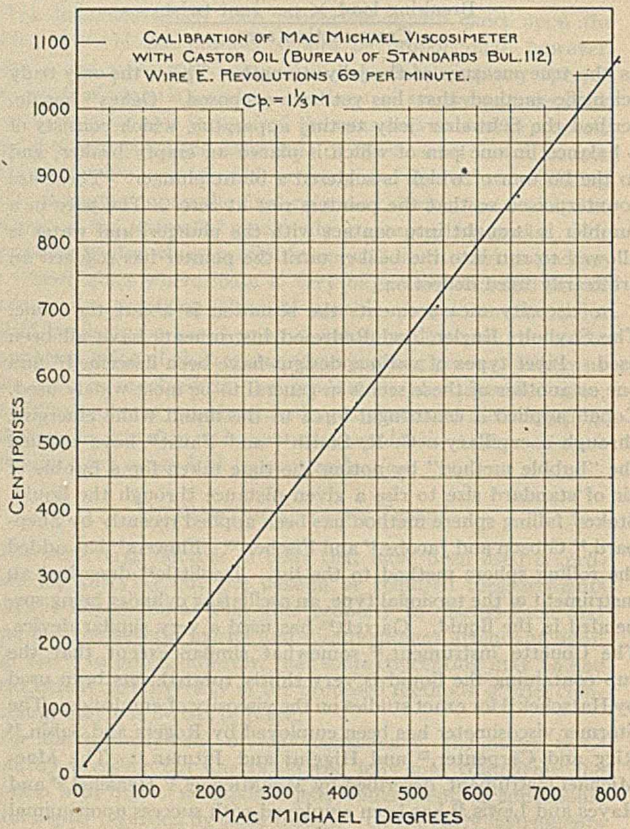
There are many methods by which the melting point may be measured, but most of these are inexact, and on account of the time required for the gel and sol forms to come to a true equilibrium, procedures intended to measure the precise temperature of melting of the jelly, or setting of the sol, are likely to be inaccurate. In an attempt to find a more rapid and accurate method for measuring this property, Bogue found that by plotting the curve of viscosity at regularly decreasing temperatures, and extrapolating to the temperature where the viscous flow would be *nil*, the figures obtained corresponded remarkably well with those obtained by several other methods of melting-point determination, both direct and indirect. But it was further observed that the same *order of differentiation* of the glues was obtained by merely taking the viscosity readings at a low temperature (32° to 35° C.). This order was, in most cases, the same as the order of viscosity at 60° C., and the order of jelly consistency at 15° C., but in all of those glues in which the viscosity was abnormal to the jelly consistency, or, vice versa, the viscosity at 32° to 35° was found to give a value intermediate between those two properties; to correspond with the true melting point; and to be precisely indicative of the gelatin content and the joint strength of the product, which was not true of any other test.*

The most satisfactory means for making this low temperature viscosity test was found to be by the use of the MacMichael viscosimeter. The advantages attendant upon the use of this instrument were found to be as follows:

1—The tests could be made very rapidly. In fact, if the glues are ready in a water bath at the proper temperature,† the viscosity tests may be made at the rate of about one per minute.

2—The instrument is a standard make, obtainable anywhere, so that its adoption would eliminate the multitudinous array of pipet and other forms of viscosimeter now in use. This would make for the standardization which is so sorely needed in glue testing practice.

3—The instrument is especially well adapted to a rapid conversion of the readings into the absolute degree of viscosity, the centipoise. The calibration of the instrument takes but a short time, and a conversion curve, which is a perfectly straight line, may be plotted, so that the MacMichael degrees may be read off in centipoises by a mere glance at the curve.‡ The centipoise unit as a standard for expressing all viscosity measurements cannot be too strongly urged. The value would be entirely independent of the size of torsion wire used, or the speed of rotation of the cup, and expresses almost exactly the specific viscosity of the material, water taken as unity, at 20 ° C.



4—Under the conditions at which the instrument would be used in glue testing, the errors, which are of considerable magnitude with many types of viscosimeter, *e. g.*, the development of turbulent flow, the increasing loss in head during the measure-

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* The temperature of 32° to 35° has been shown by C. R. Smith and by R. H. Bogue to be especially significant. Smith found this to be the temperature above which the gel form could not exist (*Loc. cit.*), and Bogue found it to be the temperature above which evidence of plastic flow could not be observed (*J. Am. Chem. Soc.*, in print).

† The glues after being soaked in the proper amount of water (see below) should be warmed to 60° C., and allowed to cool to 35° before taking the viscosity. If they are not thus preliminarily heated the readings will be erratic and unreliable, no matter how tested.

‡ The conversion curve of the instrument employed by the writer, with the use of wire number E and at a speed of 69 revolutions per minute, is shown in the accompanying figure. Castor oil was used at the advice of the Bureau of Standards, as the calibrating liquid, the absolute viscosity of which at varying temperatures is given in the U. S. Bureau of Standards *Tech. Paper* **112** (1919), 24. For the convenience of the reader, a part of the data there presented is given herewith:

Absolute Viscosity of Castor Oil

Temperature	Viscosity in Centipoises
18	1162.5
20	986
22	834
24	706
26	604
28	521
30	451
32	394
34	340
36	294
38	258
40	231
65.6	60.5
100	16.9

Each instrument with any given wire and speed must be separately calibrated, but since the curve is a straight line, only three or four different temperature readings are required. By using wire No. 27 and adjusting to a speed of about 56.5 r. p. m., the absolute viscosity in centipoises could be read directly.

ment, inconstant and faulty drainage, the change of temperature during measurement, the abnormal values obtained when insoluble material, such as zinc oxide, is present, etc., are almost entirely eliminated. The straight line nature of the conversion curve also makes for greater accuracy in computing the absolute viscosity from the instrument reading, and by a proper adjustment of the wire and the speed of rotation the absolute viscosity in centipoises may be read directly.

A RATIONAL SYSTEM OF EVALUATION

Our discussion has shown, therefore, that the gelatin content of a glue or gelatin, and also the joint strength of a glue, may be correctly indicated by a melting-point determination, while neither may be correctly assumed to be, in all cases, proportional to either the jelly consistency or the viscosity at 60° C. alone. Inasmuch as the primary evaluation of the material should be based upon some fundamental and scientifically selected property or properties, it seems that gelatin content and joint strength should be chosen. It is especially happy that these two properties are parallel. Since the *melting point* has been shown to indicate the gelatin content and the joint strength, it seems that this determination, either directly or indirectly made, should be selected as a measure of the fundamental constitution and properties of the material. The measurement of the *viscosity of a 20 per cent solution at 32° to 35° C.* by means of the MacMichael viscosimeter has been shown to be especially well adapted as an indirect estimation of the differentiation of glues and gelatins in the order of their melting points.

Different grades of glues and gelatins normally vary in water content from about 10 to 17 per cent, the higher grades retaining the larger amount of water. Of even greater importance in evaluation is the ability of any given sample of any grade to take up or lose water according to the humidity and temperature of storage. Glues have been found to vary in water content from 9 to 18 per cent from this cause alone.

It is obvious, therefore, that a 20-g. sample may contain between 16.4 and 18.2 g. of dry glue, and since this is made, for the viscosity test, to 100 g. with water, the percentage of dry glue used in the tests will vary between 16.4 and 18.2 per cent. This is sufficient to modify very seriously the viscosity or any other test made which varies with the concentration. In order to eliminate this uncertain variable it is necessary to make a moisture determination before weighing up the samples for further tests, and it is suggested that the amount of glue to be used for the viscosity test be stipulated as the equivalent of 18 g. of dry glue made up to 100 g. with water. The temperature of 35° is probably preferable to 32° as there is less change in viscosity with time at the higher value.

If this test be accepted for the above-stated purpose, it follows that the tests for jelly consistency and for viscosity at 60° C. are no longer of service for *primary* evaluation, and may be safely discarded as such. They may, however, be of great value in *secondary* evaluation, *i. e.*, in determining the adaptability of a given glue to a given service. For example, the jelly consistency would be of value in selecting glues for printers' rollers, and the rapidity of setting of the jelly as well as the viscosity at working temperatures would be desirable data for the woodworking industry.

Another test which recent investigation has shown to be of considerable importance in determining the properties of a glue or gelatin is the *H-ion concentration*.[71] If the pH value is 4.7 the viscosity, swelling, etc., are low, and the product nearly insoluble. On either side of this point these properties increase very considerably, attaining their maximum on the acid side at pH = 3.5, and on the alkaline side at pH = 9.0. At greater acidity than pH = 3.5 or at greater alkalinity than pH = 9.0 these properties again decrease. The pH value indicates therefore not only the reaction of the material, and the degree of acidity or alkalinity, but also the proximity of the substance to the points of maximum or minimum properties. The measurement may be made by either electrometric or colorimetric means.[72] One per cent solutions are best used in either case, and the results expressed in terms of pH to the nearest tenth.

The methods that may be employed for the estimation of the secondary properties should likewise receive attention that the results may be expressed in uniform terms. The *jelly consistency* test is perhaps most conveniently made by the use of the instrument described by the Forest Products Laboratory[15] and expressed in millimeters of depression, although for some more exacting requirements, as in the selection of gelatin for photographic purposes, the more elaborate and scientific method of Sheppard[26] may be used to advantage. The *viscosity* at working temperatures, 60° C., may be made with the MacMichael viscosimeter upon an 18 per cent solution (dry basis) and the results expressed either in centipoises, or, following the suggestion of Kahrs, in pounds of dry glue which, when made up to a weight of 100 lbs. with water, will produce a solution of a given standard viscosity at 60° C. as, for example, 600 centipoises. The *foam test* may be made upon the same solution in a standard glass, by means of an egg beater turned at a stated velocity of about four revolutions per second for 30 sec., and measured after 10 sec., as millimeters of foam. The *grease test* may usually be made with sufficient satisfaction by making a streak of the glue, to which a dye such as turkey red has been added, on a sheet of paper. Better still, the glue may be mixed with the calcimine or color base with which it is intended to be used, and streaks made on paper. The *appearance* may be specified according to the information desired. The form of the product as flake, sheet, ribbon, foil, or ground, should be noted. If the glues have been treated to produce a clear light product, the degree of clarity and color should be indicated. This may usually be done with sufficient satisfaction by such terms as light, clear, medium, amber, etc., or by numerical designations as No. 1, No. 2, etc. Exact color data are best obtained by the elaborate instrument of the Eastman Kodak Company. If the glue is colored, or crazed, or presents any particular property, it should be mentioned. The *odor* should be noted in the warm solution, and a strong or sour odor should not develop, in good glues, within 48 hrs., at 30° to 40° C.

In some cases special tests will be required, as for *ash*, *precipitation with aluminium salts*, etc.; in the case of gelatin for edible purposes *copper*, *zinc*, *arsenic*, and *sulfur dioxide* may be determined, and in some cases qualitative tests for *preservatives* are necessary. These are made in accordance with the customary scheme for the examination of foods, as set forth in the official publications of the Association of Official Agricultural Chemists,[73] and need not be repeated here.

For the purpose of fixing an abstract valuation, or for the estimation of tariff duties on imports, the primary evaluation only need be made.

DIFFERENTIATION BETWEEN EDIBLE GELATIN AND GLUE

The methods in common use for distinguishing between edible gelatin and glue are based upon a few tests that are admittedly inadequate. The material is examined for copper, zinc, and arsenic, the maximum permissible in edible gelatin being 30, 100, and 1.4 p. p. m., respectively. The total ash is determined, the assumption being that a glue is usually higher in ash than a pure gelatin. The jelly consistency is noted, it being assumed that a glue will show much lower values for this property than gelatin. And the general appearance, color, and odor are noted, only reasonably clear and perfectly sweet gelatin being passed favorably. Sulfur dioxide is sometimes determined, but its presence is permitted in reasonable amounts. A bacteriological examination might be of value as an additional test, but many instances have been met where a gelatin gave off an offensive odor, but was found to be practically sterile. In such cases the decomposition had obviously taken place at some stage in the manufacture, but had subsequently been stopped, probably by the addition of a germicide. A periodical inspection of the care and sanitation exercised in the several steps of manufacture and in the selection of the stock used would probably be more valuable as a basis for passing upon gelatin than any chemical or other tests upon the product that could be made. Provided, however, that a gelatin passed the requirements as an edible product, then its evaluation as a gelatin should be determined primarily, as in the case of glues, upon its content of the unhydrolyzed protein, or, which has been shown to be the same, upon the melting point or viscosity at 35° C.

Designation of Grade

The grade designation of the product, as ascertained by the primary evaluation, may conveniently be expressed by consecutive numbers, 1 being the lowest, following the name or initial letter of the type of product. Thus hide glues may be designated as Hide Glue No. 1, Hide Glue No. 2, or H_1, H_2, and so on up to perhaps H_{15}, and bone glues as Bone Glue No. 1 or B_1, to Bone Glue No. 15 or B_{15}. If the primary evaluation is measured, as suggested, by a determination of the viscosity in centipoises of an 18 per cent solution (dry basis) at 35° C., H_1 or B_1 will correspond to a viscosity of less than 20 centipoises, and, H_{15} or B_{15} to above 150 centipoises. The arrangement might well be along the lines shown in Table III.

Table III—Designation of Grade

Designation	Viscosity of 18 Per cent Solution (Dry Basis) at 35° C., in Centipoises
H_1 or B_1	Below 20
H_2 or B_2	20 to 29
H_3 or B_3	30 to 39
H_4 or B_4	40 to 49
H_5 or B_5	50 to 59
H_6 or B_6	60 to 69
H_7 or B_7	70 to 79
H_8 or B_8	80 to 89
H_9 or B_9	90 to 99
H_{10} or B_{10}	100 to 109
H_{11} or B_{11}	110 to 119
H_{12} or B_{12}	120 to 129
H_{13} or B_{13}	130 to 139
H_{14} or B_{14}	140 to 149
H_{15} or B_{15}	150 to 159
Etc.	

Obviously the highest grades would be attained only by the very pure gelatins, while only the material that was exceedingly poor would reach the lowest designation. Both classes of glues, *i. e.*, the hide and bone types, would be rated upon the same standard, but the initial letter or name would serve the desirable purpose of differentiating between the type of stock used. Edible gelatins could be referred to, if desired, as G_{12}, G_{14}, etc., but the numerical designations should always refer to a standard viscosity or other value fixed as the primary standard for evaluation.

The laboratory test sheet would appear about as indicated in Table IV.

Advantages of Proposed System

The advantages of such a system, or of any other that secures a real standardization based upon fundamental and scientific principles, are strikingly apparent. Where the jelly consistency is taken as the basis of determining grade, a set of "standard" glues must be maintained, and in the course of a few years these standard types, through occasional renewal, must inevitably alter. Furthermore, the curves for the jelly consistency of various glues at varying temperatures are not parallel, but a glue that is weaker than the standard at 10° may be the stronger at 15°. There is surely no good reason why the tests should be made at one temperature in preference to any other, but the decision upon this very arbitrary point determines the rating which a glue may receive by the current methods.

Mention has already been made of the diversity of instruments used in making the viscosity test, and the impossibility, without profound instrumental corrections, of expressing the readings obtained in terms of absolute viscosity, or any other kind of viscosity that will be intelligible to a person using any other instrument.

And most important of all, the figures obtained by the jelly strength and the high-temperature viscosity methods do not give data which are invariably expressive of any fundamental property.

These objections the proposed changes seek to remedy. The primary evaluation involves the use of no arbitrarily selected "standard" glues, but gives results that are in themselves complete without reference to any other hypothetical product. The use of a standard instrument which readily permits the employment of absolute degrees enables the readings to be understood universally, and the data obtained are indicative of fundamental properties of the material.

The grade designated is simple and very easily understood. The letter referring directly to the type of stock, and the number to the absolute viscosity, reduces to the vanishing point any mystery connected with glue grades, and enables the layman to define a glue with nearly the same degree of intelligence as may be exercised by the expert.

Bibliography

1—*Bur. Chem., Bull.* **109**, revised (1910), 54.
2—R. L. Fernbach, "Glues and Gelatine," New York, **1907**, 4.
3—J. Alexander, *J. Soc. Chem. Ind.*, **25** (1906), 158.
4—F. Kahrs, International Fisheries' Congress, Bergen, Norway, **1898.**
5—L. A. Thiele, Personal communication.
6—J. Fels, *Chem.-Ztg.*, **21** (1897), 56; **25** (1901), 23.
7—V. L. Cerri, Report to Italian Military Aviation Board, **1920.**
8—E. G. Clayton, *J. Soc. Chem. Ind.*, **21** (1902), 670.
9—R. L. Fernbach, *Loc. cit.*, **47.**
10—Lipowitz, "Neue Chemische Technologische Untersuchungen," Berlin, **1861**, 37.
11—R. Kissling, *Chem.-Ztg.*, **17** (1893), 726; **22** (1898), 171.
12—Valenta, *Ibid.*, **33** (1909), 94.
13—Scott, *Chem. Eng.*, **5** (1907), 441.
14—Sindall and Bacon, *Analyst*, **39** (1914), 20.
15—*Forest Products Lab. Tech. Notes*, **F 32** (1919).
16—E. S. Smith, U. S. Patent 911,277, February 2, 1909.
17—E. Hulbert, *J. Ind. Eng. Chem.*, **5** (1913), 235.
18—W. H. Low, *Ibid.*, **12** (1920), 355.
19—C. R. Smith, *Ibid.*, **12** (1920), 878.
20—Sheppard, Sweet and Scott, *Ibid.*, **12** (1920), 1007.
21—E. T. Oakes, 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

Table IV—Glue and Gelatin Test Sheet

Lot————

Date————

Physical Tests									Chemical Tests						
Designation No.	Designation Grade	Viscosity in Centipoises at 35° C. 18 Per cent Soln.	pH 1 Per cent Soln.	Jelly Consistency Mm. Depression 10° C. 18 Per cent Soln.	Foam Mm. 18 Per cent Soln.	Grease	Appearance	Odor	Moisture Per cent	Ash Per cent	Copper P. p. m.	Zinc P. p. m.	Arsenic P. p. m.	Sulfur Dioxide Per cent	Remarks Special Tests
49440	H_7	72	5.7	4.2	14	....	Dark, flake	Sweet	12.7	....	..	...	...	....	....
50214	H_4	46	6.9	8.1	28	....	Brown, flake	Sour	11.0	....	..	...	...	....	....
46621	B_9	90	3.7	4.1	..	....	No. 1 Sheet	Sweet	14.2	....	..	...	...	....	No. ppt. with alum
46602	B_1	17	4.9	Liquid	8	Present	Crazed, flake	Strong	10.4	....	..	...	...	....	....
80441	G_{13}	130	6.8	2.1	10	Absent	Light, ground	Sweet	16.2	1.82	10	20	0.0	.0102	O. K.
50266	B_7	78	5.4	...	13	....	White, flake	Sweet	12.2	8.7	..	...	...	....	....
70222	G_{15}	156	7.1	1.2	..	Absent	Amber, ground	Sweet	17.3	3.31	10	220	7	.027	Technical only

Performed by————

Approved by————
Chemist

22—J. Fels, *Loc. cit.*; F. Kahrs, "Glue Handling," East Haddam, Conn., **1905-6**, 58; R. Fernbach, *Loc. cit.*, 38; J. Alexander, *Loc. cit.*; National Advisory Committee on Aeronautics, *Report* **66** (1920), 26.

23—W. C. Cope, *J. Ind. Eng. Chem.*, **9** (1917), 1046.

24—C. R. Smith, *J. Am. Chem. Soc.*, **41** (1919), 135.

25—O. Faust, *Z. physik. Chem.*, **93** (1919), 758.

26—S. E. Sheppard, *J. Ind. Eng. Chem.*, **9** (1917), 523.

27—Gibson and Jacobs, *J. Chem. Soc.*, **117** (1920), 473.

28—R. Fischer, *Chem.-Ztg.*, **44** (1920), 622.

29—A. E. Fellows, *Proc. Am. Soc. Test. Materials*, **14** (1914), 565.

30—Doolittle, *J. Am. Chem. Soc.*, **15** (1893), 173.

31—Garrett, *Phil. Mag.*, [6] **6** (1903), 374.

32—Couette, *J. phys.*, **9** (1890), 414; *Ann. chim. phys.*, **6** (1890), 21, 502.

33—E. Hatschek, *Trans. Faraday Soc.*, **9** (1913), 80.

34—A. Rogers and A. Sabin, *J. Ind. Eng. Chem.*, **3** (1911), 737.

35—G. Rigg and J. Carpenter, *Ibid.*, **4** (1912), 901.

36—E. Higgins and E. Pitman, *Ibid.*, **12** (1920), 587.

37—R. MacMichael, *Ibid.*, **7** (1915), 961.

38—W. H. Herschel, *Ibid.*, **12** (1920), 282.

39—Hayes and Lewis, *J. Am. Soc. Mech. Eng.*, **38** (1916), 626, 1002.

40—R. H. Bogue, *Chem. Met. Eng.*, **23** (1920), 61, 197.

41—H. F. Zoller, *J. Ind. Eng. Chem.*, **12** (1920), 1171; *J. Gen. Physiol.*, **3** (1921), 635.

42—Chercheffski, *Chem.-Ztg.*, **25** (1901), 413.

43—Kissling, *Z. angew. Chem.*, **16** (1903), 398.

44—Winkelblech, *Ibid.*, **19** (1906), 1260.

45—Küttner and Ulrich, *Z. öffentl. Chem.*, **13** (1907), 121.

46—Herold, *Chem.-Ztg.*, **34** (1910), 203.

47—C. F. Sammet, *J. Ind. Eng. Chem.*, **10** (1918), 595.

48—A. Clark and L. DuBois, *Ibid.*, **10** (1918), 707.

49—C. R. Smith, *J. Am. Chem. Soc.*, **41** (1919), 146.

50—S. E. Sheppard and S. Sweet, *J. Ind. Eng. Chem.*, **13** (1921), 423.

51—F. Khars, *Glue*, **1** (1910), No. 3, 4; No. 4, 5; No. 5, 8; No. 6, 10.

52—A. H. Gill, *J. Ind. Eng. Chem.*, **7** (1915), 102.

53—M. Rudeloff, *Mitt. kgl. Materialprüfungsamt*, **36** (1918), 2; **37** (1919), 33.

54—National Advisory Committee for Aeronautics, *Report* **66** (1920), 21.

55—See A. Heineman, *Chem.-Ztg.*, **24** (1900), 871; J. Welmers, *Veneers*, **14** (1920), 35; R. H. Bogue, *Chem. Met. Eng.*, **23** (1920), 197.

56—Setterberg, *Schwed. Tech. Tidskrift*, **28**, 52.

57—G. Hopp, *J. Ind. Eng. Chem.*, **12** (1920), 356.

58—See Shattermann, *Dinglers polytech. J.*, **96** (1845), 115; Reardon, "Something about Glue," **1910**.

59—C. Stelling, *Chem.-Ztg.*, **20** (1896), 461.

60—F. Jean, *Ann. chim. anal.*, **2** (1897), 85.

61—F. Gantter, *Z. anal. Chem.*, **32** (1893), 413.

62—A. Müller, *Z. angew. Chem.*, **15** (1902), 482.

63—Halla, *Ibid.*, **20** (1907), 24.

64—Trunkel, *Biochem. Z.*, **26** (1910), 458.

65—Berrar, *Ibid.*, **47** (1912), 189.

66—Fahrion, *Z. angew. Chem.*, **8** (1895), 529.

67—Mavrojannis, *Z. Hyg.*, **45** (1904), 108.

68—Greifenhagen, König and Scholl, *Biochem. Z.*, **35** (1911), 217.

69—S. Trotman and J. Hackford, *J. Soc. Chem. Ind.*, **23** (1904), 1072.

70—R. H. Bogue, *Chem. Met. Eng.*, **23** (1920), 105, 154.

71—See J. Loeb, *J. Gen. Physiol.*, **1** (1918–19), 39, 237, 363, 483, 559; **3** (1920–21), 85, 247, 391; R. H. Bogue, *J. Am. Chem. Soc.*, **43** (1921), 1764.

72—See W. M. Clark, "The Determination of Hydrogen Ions," Baltimore, **1920**.

73—Assoc. Official Agr. Chem., "Methods of Analysis," 2nd edition, **1920**, 147.

Potash from Kelp[1,2]

VI—The Decolorizing Action of Adsorptive Charcoals

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The theory that the decolorizing action of charcoals is due primarily to the presence of an organic nitrogenous compound in charcoal is not upheld. On the other hand, the impurities in a charcoal are frequently responsible for many peculiar effects usually ascribed to "charcoal."

The adsorption theory of dyeing is reviewed briefly, and applied to the decolorization of sugar sirups and cottonseed oil by charcoal.

THE extreme difficulty of preparing a charcoal[3] absolutely free from oxygen, hydrogen, nitrogen, and other impurities perhaps led to the belief that these impurities were essential to give charcoal the property of decolorizing various solutions.[4] Patterson[5] was one of the early advocates of such a theory, and his work has had acceptance even up to the present.[6] It has been suggested recently by Bancroft[7] that Patterson's work be repeated. This has been done by Hall[8] who confirmed Patterson's results. The latter isolated an organic nitrogenous material of gelatinous nature from boneblack, and claimed that this substance was chiefly responsible for the decolorizing action of bone char. He calculated that this nitrogenous compound was from sixteen to forty times as active a decolorizer as the original char. The fact that wood charcoals contain practically no nitrogenous substance and have very little decolorizing power he took as further evidence in support of his theory.

Recently a number of charcoals of vegetable origin, including kelpchar, the decolorizing carbon manufactured from the Pacific Coast kelp,[9] *Macrocistis pyrifera*, have been prepared which have many times the decolorizing efficiency of bone char, and yet do not contain this supposedly essential nitrogenous constituent. The argument might be advanced, however, that these charcoals possessed superior activity in spite of this fact.

One of the objectives at this Laboratory was to activate kelpchar as highly as possible, and as a part of this investigation it was necessary to determine just how important it was to have present Patterson's nitrogenous compound.

Patterson isolated the compound by treating 1 g. of purified boneblack first with a few cc. of cold concentrated sulfuric acid. The acid dissolved a substance which imparted a brown color to the solution. After separating the acid from the residue and diluting it with 10 to 12 volumes of water, a gelatinous precipitate was formed which settled with difficulty. The char was treated with a second and a third portion of acid, these times the acid being hot. In each instance a brown gelatinous precipitate was produced on dilution of the acid. If the acid became too dilute as a result of attempts to wash the precipitate, the latter would not settle. Patterson added the acid suspension to a caramel solution and diluted to a definite volume. When the precipitate settled he compared the supernatant liquid colori-

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[1] Received January 4, 1922.

[2] Published with the permission of the Secretary of the Department of Agriculture.

[3] Bancroft, *J. Phys. Chem.*, **24** (1920), 127, 201, 342.

[4] Glassner and Suidu, *Ann.*, **361** (1908), 351; Knecht and Hibbert, *J. Soc. Dyers Colourists*, **32** (1916), 226.

[5] *J. Soc. Chem. Ind.*, **16** (1903), 608.

[6] C. F. Bardorf, *Facts about Sugar*, **11** (1920), 351; W. D. Horne, *Ibid.*, **11** (1920), 372.

[7] THIS JOURNAL, **13** (1921), 155.

[8] *Ibid.*, **14** (1922), 18.

[9] THIS JOURNAL, **10** (1918), 812; **11** (1919), 864.

metrically with a standard caramel solution of equal dilution. The decrease in color in one instance amounted to 33.3 per cent and in another to 42.4 per cent. The precipitated organic matter in the first experiment was 0.0198 g. and in the second 0.010 g. Since an equal volume of diluted caramel solution would be completely decolorized by 0.9542 g. of boneblack, Patterson calculated the organic constituent of boneblack to be from 16.03 to 40.46 times better as a decolorizer than the char itself.

The refinement of these calculations would infer a much greater degree of precision in experimental work than would seem to be justified by the wide difference in the two results. Patterson excuses this disagreement by pointing out that the extractions were made at different temperatures, and that different bodies were extracted which had decolorizing characteristics peculiar to themselves. Another explanation of his results is given below.

DECOLORIZING ACTION OF ACID

It will be noticed that Patterson made no attempt whatever to duplicate conditions regarding acidity when comparing the decolorizing efficiencies of boneblack and the several gelatinous suspensions. Such a precaution is very necessary, as was pointed out in a previous paper,[10] and the neglect of this precaution may possibly explain the apparently anomalous behavior of charcoal in different solutions, as well as the extravagant claims of some charcoal patentees of to-day. It was suspected that the remarkable decolorizing power of Patterson's suspensions was due, not to the few milligrams of the solid material, but to the acid in which they were suspended. This supposition was confirmed by the following test:

A neutral caramel solution was prepared of a concentration such that 1 cc., after being diluted to 100 cc., would be decolorized by 1 g. of the best decolorizing boneblack on hand. A quantity of this weaker standard solution was made up, and to 100 cc. of it was added one drop of concentrated sulfuric acid. Comparison with the original solution showed that the acid had caused a decrease in color amounting to 25 per cent. More acid caused more color to disappear, although the solution did not become colorless even with considerable excess acid.

These facts afford a much simpler explanation of Patterson's results and easily account for the wide divergence in decolorizing values of his suspensions, it being highly improbable that the same amount of acid was added to the caramel solution in each instance.

Patterson did not show that the decolorizing property of charcoal was diminished by the removal of the organic body. He may have attempted to do this and failed, as did the present writer, because concentrated sulfuric acid so altered the form and character of the char that strictly comparable results with the initial and final char could not be made.

The view that acid caused the decolorization of the caramel solution and not the gelatinous precipitate receives further support from Patterson's own observations: that the precipitate suspended in acid was a good decolorizer, whereas the dried precipitate possessed practically no decolorizing power.

It is not intended that these remarks should support the view that the impurities in a charcoal have no influence on the decolorizing action, as quite the contrary is usually true. What is desired is to emphasize that charcoal is a complex substance, and that the impurities in it may or may not play an important role when a charcoal (or gelatinous precipitate) decolorizes a solution. Sometimes these impurities act adversely, and sometimes coöperatively with a charcoal. On some occasions they may be without influence at all.

Thus, if salts or oxides of iron be present in a charcoal, and such a charcoal be added to an unbleached citric acid solution, the iron will react with some of the impurities of the solution and form very highly colored compounds. Although the charcoal adsorbs a portion of these compounds, the amount left behind may be so highly colored that the solution appears more colored than the original.

Further, a charcoal may contain free acid. Then on being added to neutral sugar sirup, a greater decolorization will be produced than if the charcoal had been neutral or alkaline.

The acid in this instance acts along three lines. In the first place, there are substances in cane sugar sirups which act like indicators, being less colored in the presence of acid than in alkali. The second effect of the acid is to lower the solubility of the color-forming compounds, thus making it easier for the charcoal to adsorb them. That such compounds exist in cane sugar sirups was shown by Zerban[11] who isolated a group of polyphenols and showed that these compounds caused much of the color of the sirup. These phenols are acidic in nature; therefore if strong acid were added to the solution their ionization would be repressed. This would cause diminished color intensity and solubility. The lessened solubility[12] would allow them to be more readily adsorbed by charcoal.

The third effect of acid is to furnish H ions for the charcoal to adsorb. H ions and OH ions are especially adsorbed by charcoal.[13] The adsorption of H ions causes the charcoal to become positively charged, and since the color radical of the phenol is negatively charged, the mutual attraction causes the solution to be decolorized.

Hydroxyl ions, having the reverse effect, make possible the use of alkali for regenerating spent "sugar charcoal."

ADSORPTION THEORY OF DYEING

The extraordinary importance which H ions and OH ions play in the decolorization of liquids by charcoal led to the conclusion that the phenomenon was the same as that exhibited by a fabric when removing dye from a dye bath. The impurities in a solution to be decolorized or deodorized are the dyes, and the charcoal is the fiber. That charcoal will act like a piece of cloth in removing dye from solution is not new to dye chemists,[14] but the application of this knowledge to the decolorization of sugar sirups and other solutions seems to have been entirely overlooked. Industrially, charcoal is applied in a most empirical manner. Much assistance could be had in setting the correct conditions for the most efficient usage of charcoal if some of the generalities of dyeing be kept in mind.

Bancroft[15] states that:

> A fiber tends to adsorb everything in solution in amounts varying with the nature, concentration, and temperature of the solution, and the nature of the fiber. * * * * A basic dye is one which contains the color in the basic radical, while an acid dye contains the color in the acid radical. * * * * In order to get the maximum adsorption of an acid dye, we should have present an ion of the opposite charge, which is readily adsorbed. In case of basic dyes, the dye should be more readily taken up in a neutral or alkaline solution. Acids (hydrogen ions) decrease the dyeing of basic dyes and increase that of acid dyes. This action is proportional to the concentration of hydrogen ions. Bases (hydroxyl ions) have just the opposite effect.

When wool is dipped in an acid dye solution such as picric acid, the quantity of dye removed will be greater the higher the H-ion concentration. If wool be made to adsorb a basic dye, such as malachite green, H ions inhibit the color removal and OH ions increase it. In this connection it might be worth while to mention that some laboratories prefer to compare charcoals by observing the decolorization produced on a dye solution such as malachite green. The importance of having identical con-

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[10] THIS JOURNAL, **14** (1922), 19.

[11] THIS JOURNAL, **11** (1919), 1034.

[12] Lundelius, *Kolloid Z.*, **26** (1920), 145.

[13] Rona and Michaelis, *Biochem. Z.*, **94** (1919), 240.

[14] Pelet-Jolivet, "Die Theorie des Farbeprossess," **1910**, 58.

[15] *J. Phys. Chem.*, **18** (1914), 1.

centrations of H ions or OH ions throughout a series of tests will now be apparent.

In a qualitative way the effect of acid and alkali on the decolorization of sugar sirups has already been described. Bradley[16] quantitatively studied the effect of acidity on the decolorization of sugar molasses and found that the decolorization was nearly proportional to the quantity of acid present. This agrees well with the above-outlined theory. He was surprised, however, to find that when equivalent quantities of both weak and strong acids were used the decolorization was nearly equal in each case. Citric or tartaric acid was just as effective as sulfuric acid. In the interpretation of these data it should be remembered that an acid is made up of two parts, and that each ion influences the equilibrium independently. Therefore, when decolorization tests are made with different acids, the result in each case will be the net result produced by the H ions and the corresponding acid ions. When citric acid is compared with hydrochloric acid, the citrate ions and chloride ions affect the equilibrium as well as the H ions. The weaker concentration of H ions afforded by the citric acid tends to cause less color to be removed than by an equivalent amount of hydrochloric acid. On the other hand, the coagulating effect of the citrate ion on the sugar colloids is much greater than that of the chloride ion. The net result of these two acids may thus be about the same.

By increasing the concentration of sugar in a molasses solution Bradley found the decolorizing efficiency to be reduced. This is not surprising when one accepts the view that adsorption is a matter of equilibrium, and that this equilibrium depends upon the nature and concentration of everything in solution. The colors are evidently more soluble in the concentrated sugar solution and therefore adsorbed to a lesser extent.

The above theory regarding the decolorization of liquids with charcoal, although based principally upon experiments made with aqueous solutions, has promise of extension to nonaqueous solutions. This is a relatively new field for charcoal and facts are none too numerous.

Cottonseed oil contains some colored impurities which on electrolysis migrate toward the negative pole. These particles are therefore positively charged and may be considered as basic dyes. Accordingly, if OH ions, or for that matter any other negatively charged ions readily adsorbed by charcoal in cottonseed oil, were added to the oil along with the charcoal, color removal should be increased. If the solution were acid, which would allow H ions to be adsorbed, removal of color would be hindered.

The latter may be demonstrated by adding a little glacial acetic acid to the oil before adding the charcoal. The acid has no apparent physical or chemical effect on the oil, but distinctly reduces the decolorizing effect of the charcoal.

It would be of interest in this connection to note the action of some material soluble in cottonseed oil, which would furnish a negative ion readily adsorbed by the charcoal. Such a condition should promote the removal of color. Direct evidence on this point is lacking, but there is a certain analogy between the action of fuller's earth and what would be expected to happen were charcoal given a negative charge. According to Glick,[17] fuller's earth becomes negatively charged when placed in cottonseed oil, and this property enables it to remove the positive colors.

Fuller's earth[18] probably owes its negative charge to the OH or other negative ions which it adsorbs strongly. The positive colors are literally dragged along and attached to the earth because of electrostatic attraction—an action similar to that of charcoal, H ions, and negative colors.

Charcoal does not show this preferential adsorption of OH ions; it adsorbs OH or H ions with equal avidity.[13] These facts are useful in explaining why fuller's earth has been used chiefly for oil purification and not for sugar, and why charcoal, except recently, has been used for sugar sirups and not oils.[19]

Suppose fuller's earth be placed in sugar sirup. If the solution be neutral or alkaline, the earth will adsorb OH ions and repel most of the color ions. If the solution be acid practically no ions will be adsorbed. On the other hand, when charcoal, comparable in activity with fuller's earth, is placed in alkaline sugar sirup, OH ions will be adsorbed, but less so than in the case with fuller's earth. There is, therefore, less repellent action on the phenols and somewhat more decolorization. The action in acid solution has already been described.

This preferential adsorption by fuller's earth of basic dyes is at least one reason why in the past it has been used instead of charcoal for oil purification. Recently charcoals such as kelpchar have been prepared whose adsorptive intensity and capacity (activity) for all ions, both positive and negative, have been so increased as to overlap the region occupied by fuller's earth. These charcoals are now being used to some extent for oil purification. Whether or not fuller's earth or materials of similar nature will have their adsorptive characteristics so developed as to compete with or displace these newer charcoals is a question for the future to decide.

In harmony with the "dye" theory of decolorizing solutions is a fact brought out by Glick that with some oils a mixture of earth and charcoal is more effective than either alone. In such a mixture the earth may be considered to be adsorbed by the charcoal, and to give the charcoal a greater negative charge than the latter could possess by itself. The additional charge allows the charcoal to make fuller use of its great surface and produces greater decolorization. Steric hindrance probably prevents the earth from utilizing its charge completely when used alone. In the language of the dye chemist, charcoal might be said to have been "mordanted" with fuller's earth. If this explanation be true it points to many interesting developments. Charcoal in the future may be expected to be mordanted with materials that will direct its action along specific lines, just as cotton is mordanted according to the dye it is expected to take up.

Just as the nature of a fiber affects the equilibrium in a dye bath, so the nature of a charcoal affects the decolorization of a solution. Charcoals differ because of the variety of raw materials from which they are derived, and because of the divers methods used in manufacture. Some charcoals will be characterized by relatively shallow capillaries, others will have longer ones.[20] The total surface area per gram of material will be different, also the number and position of "elementary spaces."[21] Steric hindrance[22] will frequently be a determining factor. The instantaneous[23] or pseudo-equilibrium as well as the final equilibrium will vary with the charcoal.

Although physical structure plays an important part in the behavior of a charcoal, its position must not be overemphasized. There are other factors just as important as, and probably more so than "cellular structure." As an example of this, a charcoal was prepared from kelp juice that had identical decolorizing characteristics of charcoal made from the body of kelp itself. Also, as a decolorizer, blood charcoal is far more powerful than many other charcoals made from materials of a more definite structure. In studying charcoal, therefore, it is well to keep in mind that it is a complex substance and that the results seldom depend upon any one characteristic.

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[16] *J. Soc. Chem. Ind.*, **39** (1919), 396.

[17] *Cotton Oil Press*, **4** (1921), 41.

[18] Cameron, *J. Phys. Chem.*, **14** (1910), 400.

[19] Sneller, *Louisiana Planter*, **59** (1917), 154.

[20] Dorsey, THIS JOURNAL, **11** (1919), 383.

[21] Langmuir, *J. Am. Chem. Soc.*, **40** (1918), 1361.

[22] Langmuir, *Ibid.*, **38** (1916), 2221; **39** (1917), 1848.

[23] McBain, *Trans. Faraday Soc.*, **14** (1919), 201; Cude and Hulett, *J. Am. Chem. Soc.*, **42** (1920), 391; Bradley, *Loc. cit.*; Lamb, Wilson and Chaney, THIS JOURNAL, **11** (1919), 420; Sheldon, *Proc. Nat. Acad. Sci.*, **6** (1920), 178; Lemon, *Ibid.*, **5** (1919), 291.

First Report of the Committee on Contact Catalysis

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(Continued)

Promoter action is by no means confined to the ammonia synthesis. Pease and Taylor[44] have collected the data on promoter action. Ipatiew[45] found that copper oxide in an iron tube was much more effective in causing the hydrogenation of amylene than was copper oxide in a copper tube. The Badische Company[46] state that hydrogenation of fats with nickel is accelerated by the presence of tellurium. Dewar and Liebmann[47] claim that a mixture of nickel and copper oxides can be reduced in the oil at 190° and will hydrogenate cottonseed oil rapidly at that temperature, whereas nickel oxide alone requires a temperature of about 250° for reduction. Hochstetter[48] found that a mixture of silver and copper was more effective for the synthesis of formaldehyde from methanol than either metal singly. Maxted[49] states that bismuth, tungsten, and copper make iron more active in the ammonia oxidation. Mixed oxides are more effective in the oxidation of carbon monoxide than any of the oxides taken singly. The phenomenon of promoter action is thus a fairly common one.

ORIENTED ADSORPTION

Though Langmuir considers adsorbed substances as held by bonds or contravalences to the adsorbing agent and though he speaks of oriented adsorption, he has never gone into details in regard to this and it is by no means certain that his conception of oriented adsorption is the same as that of an organic chemist, for instance. For the moment it looks as though the organic chemist were the safer man to follow. The immediate problem is to devise methods of telling what particular bonds or contravalences are effective in causing the adsorption of ethyl acetate, for instance, by any given catalytic agent. Having done that we must show that the opening up of those particular bonds or contravalences are the necessary prerequisite to the reaction which is produced by that particular catalytic agent. When this has been done, the next problem will be to develop a theory which will enable us to predict that a given catalytic agent will cause such and such bonds or contravalences to open; but that lies quite a way in the future. It must also be remembered that, for the other type of contact catalysis, the identification of the intermediate compounds does not account for the catalytic action. On the other hand, it is impossible to take the next step until the intermediate compounds have been identified.

If we adopt the hypothesis that part, at any rate, of the catalytic action of a given adsorbent is due to oriented adsorption, it is clear that we may have an adsorbent slowing down the reaction in case the orientation is unsatisfactory. This seems to have been realized by Kruyt and van Duin.[50] They find that the following reactions are retarded by charcoal although the reacting substances are adsorbed by it: the saponification of ethyl acetate and of sodium methyl-benzoate-*p*-sulfonate; the addition of bromine to the acid sodium salt of *p*-sulfo-cinnamic acid; the removal of bromine from the neutral and the acid sodium salts of *p*-sulfonic-dibromohydrocinnamic acid by means of potassium iodide. On the other hand, the removal of bromine from α,β-dibromopropionic acid by means of potassium iodide is accelerated by the presence of charcoal.

The authors conclude from these results that adsorption involves more than a mere increase of concentration at the surface.

> This conclusion is quite in harmony with the theories of Langmuir,[51] and Harkins[52] and his collaborators. In addition to a surface concentration there is also an orientation. This latter may cause a decrease in the reaction velocity. If the two adsorbed, reacting substances are not free in their movements, their chances of encountering one another are decreased, and the probability that they will get into a state favorable to the reaction may be changed for the worse.
>
> There is yet another reason why the reaction may be checked. At the surface between water and a phase consisting of carbon or of carbon compounds, the molecules will turn their more polar portion towards the water. If the reaction takes place at a nonpolar, or less polar, portion of the molecule, this part is turned away from the aqueous phase and from the substances dissolved in it. If the two reacting substances are more or less polar, it may be that they will be adsorbed in such a way that the reacting portions are turned away from each other. From this point of view, it is clear why we obtained a negative catalysis at first in spite of the adsorption. It is true that the aromatic substances are adsorbed strongly; but in order to make them soluble we had introduced the radical SO_3Na. This radical increases the solubility very much and is also highly polar.
>
> We can therefore form the following conception as to the position taken by the molecules at the surface between the charcoal and the liquid. In the acid sodium salt of *p*-sulfocinnamic acid we have the following arrangement.[53] The benzene ring with three double bonds tends to place itself horizontally on the surface; but this is interfered with by the polar groups in the para position. In view of the strongly acid character of the sulfonic acids and especially in view of their effect in increasing the solubility, the radical SO_3Na is undoubtedly more polar than the radical $CH:CH.CO_2H$. The first tends to draw the portion of the benzene ring to which it is attached into the water, which means that the other is pushed toward the charcoal. It is, however, this unsaturated side chain which reacts with the bromine. In the case of sodium methyl-benzoate-*p*-sulfonate, the organic side chain is in a disadvantageous position. The small molecules of adsorbed bromine or caustic soda (or perhaps the free sodium and hydroxyl ions) will undoubtedly all be at the water surface and will find turned from them the radicals with which they should react.[54] The dissolved and unadsorbed molecules of bromine and of sodium hydroxide are handicapped in the same way. In spite of the increased concentrations the conditions at the surface of the adsorbent are unfavorable to the progress of the reaction and out in the solution the reaction goes more slowly because of the decreased concentrations there in consequence of adsorption.
>
> The situation is undoubtedly as follows in the case of ethyl acetate. In the molecule $CH_3CO.C_2H_5$ the radical $C:O$ is unquestionably the most polar and it is probably the doubly tied oxygen which sticks out into the water and the ethoxy group OC_2H_5 is consequently more or less buried.
>
> We tried at first to increase the polar character of the cinnamic acid radical. The acid sodium salt of the *p*-sulfonic-dibromohydrocinnamic acid is more soluble in water than the corresponding compound containing no bromine, and since the bromine increases the solubility of the compound it must increase the polarity of the group. The remarkable reaction of the bromine addition compound with potassium iodide made it seem probable that the bromine atoms had brought the side chain out enough to make it react with the potassium iodide in solution.[55]

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[44] *J. Phys. Chem.*, **24** (1920), 241.

[45] *Ber.*, **43** (1910), 3387.

[46] D. R. P. 282,782 (1913).

[47] U. S. Patents 1,268,692; 1,275,405.

[48] U. S. Patents 1,100,076; 1,110,289.

[49] *J. Soc. Chem. Ind.*, **36** (1917), 777.

[50] *Rec. trav. chim.*, [4] **2** (1921), 249.

[51] *J. Am. Chem. Soc.*, **38** (1916), 2221; **39** (1917), 1848.

[52] *Ibid.*, **39** (1917), 354, 541.

[53] Harkins, Davies and Clark, *Ibid.*, **39** (1917), 582.

[54] [Since bromine is much more soluble in organic liquids than in water, this does not necessarily follow.]

[55] [Since potassium iodide is adsorbed strongly by charcoal, the reaction may be with the adsorbed iodide and not with the dissolved iodide.]

> In order to make doubly sure, the radical COOH was converted into COONa. Since the results were negative we concluded that the polar effect of SO_3Na was still preponderant. * * *
>
> Since it was difficult to avoid the radical SO_3Na in reactions with aromatic compounds in aqueous solutions and since its polar character often turns the scale, we tried to find some other method of escaping from this dilemma. According to Harkins we should have better prospects of success if we selected a suitable aliphatic compound. The criteria seemed to be met by the α,β-dibromopropionic acid. There is a polar effect at each one of the three carbon atoms and, according to the theory of Harkins, the chain of carbon atoms should seek a position parallel to the boundary surface, so that the three polar groups would turn to the water. It was possible of course that one of the groups, COOH or Br, would be the more powerful and would make the carbon chain asymmetric; but, even so, the conditions were much more favorable than in the preceding experiments with sulfonated aromatic compounds. As a matter of fact, charcoal does accelerate the reaction.

POISONS

While we are still very much at sea as to any satisfactory theory of contact catalysis, matters are in much better shape in regard to what was at one time a most mysterious phenomenon—the poisoning of the catalytic agent. On any theory of contact catalysis except radiation at a distance, the reaction takes place in or at the surface of the catalytic agent. A necessary consequence of this is that any substance, which cuts down the rate at which the reacting substances reach the catalytic surface[56] or which prevents them from reaching it,[57] will decrease the reaction velocity and may destroy the catalytic action entirely. Berliner[58] has shown that traces of fatty vapors from the air or from the grease on the stopcocks will decrease the adsorption of hydrogen by palladium from about nine hundred volumes to nothing. Pollard has observed a similar decrease with platinized asbestos from about one hundred and forty volumes to a negligible amount. Faraday[59] proved that traces of grease destroy the catalytic action of platinum black. Lunge and Harbeck[60] found that carbon monoxide inhibits practically completely the catalytic action of platinum on a mixture of ethylene and hydrogen. Taylor and Burns[61] conclude from their experiments that "even when pressures of carbon monoxide not exceeding a few centimeters exist, it is reasonable to suppose that the platinum surface remains covered so thoroughly with carbon monoxide that hydrogen or other gases are unable to reach it." They also point out that platinum which holds carbon monoxide so tenaciously is not a good catalytic agent for the reduction of carbon monoxide to methane, whereas this reaction takes place readily with palladium from which carbon monoxide can be removed readily by hydrogen at ordinary temperatures.

Schönbein[62] pointed out that the hydrides of sulfur, tellurium, selenium, phosphorus, arsenic, and antimony act very energetically in cutting down the action of platinum on mixtures of air with hydrogen or ether. Since he did not realize that an adsorbed gas film might keep out other gases, he decided that the hydrides must decompose, giving rise to a solid film. This hypothesis is not necessary to account for the phenomenon; but he was right in at least one case, for Maxted[63] has found that hydrogen sulfide is decomposed by platinum black with evolution of hydrogen and that the sulfurized platinum does not adsorb hydrogen. Maxted[64] has also studied the poisoning action of lead on platinum. The effect is apparently proportional to the amount of lead, 1 mg. of lead neutralizing or paralyzing 8.8 mg. of platinum. Paal and Steger[65] have shown that mercury displaces hydrogen from a palladium hydrosol. Langmuir[66] believes that oxygen prevents the dissociation of hydrogen by a heated tungsten filament because it cuts down the adsorption of the hydrogen. He states that:

> The action of oxygen preventing the dissociation of hydrogen by a heated tungsten filament is clearly that of a catalytic poison. It has been shown previously[67] that the dissociation of hydrogen takes place only among hydrogen molecules adsorbed on the surface of the tungsten. The only way in which oxygen can prevent such action in a high vacuum is by the actual presence of oxygen atoms on the surface. Since the dissociation at 1500° K. is entirely prevented by the oxygen, and since the range of atomic and molecular forces does not exceed the dimensions of the atoms, it must follow that much more than half the surface must be covered by oxygen atoms or molecules. For if the surface were only half covered, then, according to probability laws, uncovered areas several times as large as the diameters of atoms would not be of rare occurrence, and on these areas dissociation could occur.

Harned[68] has shown that the rate of adsorption of chloropicrin by a charcoal which has been cleaned by washing with chloropicrin is much greater at first than by a charcoal which has not been so cleaned, although the final equilibrium is apparently about the same in the two cases. This is analogous to the evaporation of water when covered by an oil film. The oil cuts down the rate of evaporation very much but has practically no effect on the partial pressure of water at equilibrium. Taylor[69] points out that normally the time of contact between a gas and the solid catalytic agent is extremely small and consequently anything which decreases the rate of adsorption will cut down the reaction velocity very much.

It is easy to see that the piling up of the reaction products will cut down the reaction velocity, if they prevent the reacting substances from coming in contact with the catalytic agent. This has been observed in the contact sulfuric acid process.[70] The explanation that the decrease in the reaction velocity is due to a decreased adsorption of the reacting substances was first given by Fink,[71] who is the real pioneer in this line. Although the reaction between carbon monoxide and oxygen is practically irreversible at ordinary temperatures, Henry[72] recognized that the presence of the reaction product might slow up the rate of reaction and he proved his point by increasing the reaction velocity when he removed the carbon dioxide with caustic potash. Water vapor checks the catalytic dehydration of ether[73] and of alcohol[74] and hydrogen cuts down the catalytic dehydrogenation of alcohol.

W. C. McC. Lewis[75] points out that the explanation of the poisoning of catalytic agents on the basis of adsorption leads to certain conclusions in regard to the temperature coefficient.

> One of the chief difficulties met with in the kinetics of heterogeneous reactions has its origin in the selective nature of the adsorbability of the reactions and the resultants, particularly the latter. The so-called catalytic poisons are now generally regarded as owing their effect to marked selective adsorption, as a result of which the surface of the catalyst becomes covered with a layer of molecules and is thus no longer capable of catalyzing the reaction. In many cases the resultants of the reactions are adsorbed in this manner and consequently function as a catalytic poison. Since the extent of adsorption diminishes as the temperature rises, it is obvious that when such poisoning effects are present, the temperature coefficient of the reaction

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[56] Taylor, *Trans. Am. Electrochem. Soc.*, **36** (1919), 149.

[57] Bancroft, *J. Phys. Chem.*, **21** (1917), 734.

[58] *Wied. Ann.*, **35** (1888), 903.

[59] "Experimental Researches on Electricity," **1** (1839), 185.

[60] *Z. anorg. Chem.*, **16** (1896), 50.

[61] *J. Am. Chem. Soc.*, **42** (1921), 1285.

[62] *J. prakt. Chem.*, **29** (1843), 238.

[63] *J. Chem. Soc.*, **115** (1919), 1050.

[64] *Ibid.*, **117** (1920), 1280, 1501; **119** (1921), 225.

[65] *Ber.*, **51** (1918), 1743.

[66] *J. Am. Chem. Soc.*, **38** (1916), 2272.

[67] *Ibid.*, **38** (1916), 1145.

[68] *Ibid.*, **42** (1920), 372.

[69] Taylor, *Trans. Am. Electrochem. Soc.*, **36** (1919), 149.

[70] Bodländer and Koppen, *Z. Elektrochem.*, **9** (1903), 566; Berl, *Z. anorg. Chem.*, **44** (1905), 267.

[71] Bodenstein and Fink, *Z. physik. Chem.*, **60** (1907), 61.

[72] *Phil. Mag.*, [3] **9** (1836), 324.

[73] Ipatieff, *Ber.*, **37** (1904), 2996.

[74] Engelder, *J. Phys. Chem.*, **21** (1917), 676.

[75] *J. Chem. Soc.*, **115** (1919), 182.

velocity over a certain range of temperatures is not comparable with that over a different range, for the total observed velocity depends only on the true effect of temperature on the chemical process itself, but likewise on the alteration in the extent of active surface presented to the reactants. The simplest conditions are obviously those in which the adsorption effects are a minimum, and such conditions will occur generally when the energy required for sublimation or desorption is small. In other cases, where adsorption effects are large, it is necessary to correct the observed velocity constants for the change in the area of the effective surface produced as a result of the change in temperature. Thus in the case in which the resultant is markedly adsorbed, and therefore acts as a negative catalyst, the temperature coefficient will possess too high a value and, instead of decreasing as temperature rises, may even increase. A similar abnormal behavior is to be anticipated when a reaction proceeds partly in the homogeneous gaseous phase, partly in the surface, for, as the temperature rises, the reaction tends to predominate in the gaseous phase, and therefore possesses a higher temperature coefficient.

We have seen that the poisoning of a catalytic agent is due to marked adsorption, which cuts down the adsorption of the reacting substances. We have also seen that the presence of sulfur trioxide tends to decrease the rate of reaction of sulfur dioxide and oxygen. We can now imagine a hypothetical case in which one of the reaction products is adsorbed so strongly that it acts as a poison. In that case we shall get entirely different results depending on the amount of catalytic agent present. If there is a large excess of catalytic agent the reaction will run to an end or to true equilibrium before the catalytic agent is entirely poisoned. If, on the other hand, there is only a small amount of catalytic agent, it will be poisoned very early in the course of the reaction, and we shall have an apparent equilibrium reached from only one side which will vary with the amount of catalytic agent. For any given amount of catalytic agent we shall get an apparently definite end-point; but the value of the end-point will vary with the amount of catalytic agent taken. At least one case of this sort has been recognized definitely. Neilson[76] has studied the splitting of salicin and amygdalin by platinum black.

It is found that the amount of splitting of salicin in a given time reached a maximum, and then with increasing time the amount of splitting was not proportional to the time, being materially less in the last twenty-four hours than it was in the preceding. This is due, no doubt, to the effect of the products of the splitting—especially the saligenin. It is more probably due, however, to the salicylic acid produced by the oxidation of saligenin to salicylic acid by the platinum. It is well known that salicylic acid has a marked retarding action on enzymes as shown by Kastle and Loevenhart[77] in its action on lipase; and by Neilson[78] in its action on platinum black in the hydrolysis of ethyl butyrate.

The experiments with amygdalin and platinum black were carried out in the same way as those with salicin. It was anticipated, however, that the amount of splitting by the action of platinum black on the amygdalin would be small, as it is well known from Bredig's work on the catalysis of hydrogen peroxide by colloidal platinum,[79] and from Neilson's[78] work on the hydrolysis of ethyl butyrate by platinum black, that hydrocyanic acid has a marked retarding action on the catalytic action of platinum. One of the splitting products of amygdalin is hydrocyanic acid; and according to the above experiments one would expect the action of platinum black on amygdalin to be retarded, if not stopped entirely. Such, indeed, was found to be the case, as the first experiment with tightly corked flasks was entirely negative. It occurred to me that by leaving the flasks uncorked the hydrocyanic acid would volatilize and the action would then proceed. This is in keeping with the well-known fact that removing one of the products of a chemical reaction allows the action to go on to completion. By leaving the flasks uncorked it was found by a qualitative test that platinum splits up the amygdalin. It was further seen that the action did not go on to completion, as the amount of sugar produced was small.

Since enzymes are poisoned by many substances in something the same way that colloidal platinum is, it seems worth while to see whether autotoxic catalysis would account for some of the peculiarities in enzyme action which have puzzled people. If autotoxic catalysis occurs, we should expect that the presence of the reaction products would cut down the reaction velocity even though the reverse reactions were negligible. If the poisoning action of the reaction products is sufficient we should get false equilibria if we started with small amounts of the enzymes and the reaction would run to an end if we took larger amounts of the enzymes. Both these phenomena have been observed.[80]

The poisoning of colloidal platinum in its action on hydrogen peroxide solutions is undoubtedly due to adsorption; but we have no direct measurements on the adsorption and consequently we do not know positively that this is the right explanation and we do not know that there may not be other factors which have been overlooked.

PROTECTING COLLOID AS POISON

One possible disturbing factor may be the presence of a protecting colloid added to stabilize a metal hydrosol.[81]

The rate of decomposition of hydrogen peroxide by colloidal platinum has been made use of in determining the absolute and relative influences of different protective colloids upon the colloidal metal,[82] the times required for the decomposition of a definite percentage of the peroxide under varying conditions being noted. With gelatin the results are typical, and are given in the following table:

Percentage of Gelatin	Relative Times Required to Decompose 50 Per cent of the Peroxide Solution
0.00	100
0.001	437
0.01	460
0.05	620
0.10	983

It will be noticed that even small quantities of gelatin exert a most important influence, retarding the decomposition of the peroxide very considerably, as is usual with a protective colloid. The gelatin, however, increases the stability of the colloidal metal solution, and tends to prolong its period of activity by preventing its precipitation by electrolytes, thereby enabling many reactions to be studied other than the decomposition of pure hydrogen peroxide solution.

Similar results have been obtained by Rideal[83] and by Iredale.[84] While these are just what might have been predicted, there is no explanation at the moment for the results of Paal and Hartmann[85] that addition of colloidal cupric hydroxide increases the action of a palladium hydrosol on oxyhydrogen gas, while addition of colloidal zinc hydroxide first retards and then increases the rate of reaction. Mercury displaces hydrogen from a palladium hydrosol[86] and decreases the catalytic action on oxyhydrogen gas. It does not destroy the catalytic action on hydrogen peroxide, presumably because mercury itself decomposes hydrogen peroxide catalytically.

EARLY VIEWS ON POISONING

It is interesting to note that as far back as 1857 Bunsen perceived clearly that the removal of the reaction products is essential to the continued action of the catalytic agent. Speaking of the catalytic action of platinum and manganese dioxide on hydrogen peroxide, Bunsen[87] says that "it is only when the products of decomposition are removed by foreign forces, such as

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[76] *Am. J. Physiol.*, **15** (1906), 148.

[77] *Am. Chem. J.*, **24** (1900), 491.

[78] *Am. J. Physiol.*, **10** (1903), 197.

[79] Bredig, "Anorganische Fermente," **68** (1900).

[80] Tammann, *Z. physik. Chem.*, **18** (1895), 426; Kastle and Loevenhart, *Am. Chem. J.*, **24** (1900), 491.

[81] Friend, "A Textbook of Inorganic Chemistry," 9-I (1920), 271.

[82] Gröh, *Z. physik. Chem.*, **88** (1914), 414.

[83] *J. Am. Chem. Soc.*, **42** (1920), 740.

[84] *J. Chem. Soc.*, **119** (1921), 109.

[85] *Ber.*, **51** (1918), 894.

[86] Paal and Steger, *Ibid.*, **51** (1918), 1743.

[87] *J. Chem. Soc.*, **25** (1873), 736.

gravitation, capillarity, expansion, etc., and by means of these foreign forces new matter is brought into contact, that the phenomenon is repeated."

Debus[88] has considered the question of effective collisions and has anticipated some of Langmuir's views on oriented adsorption.

> Whenever two mols of peroxide of hydrogen meet in the *position of reaction*, then decomposition into water and oxygen will take place, but if they collide in other positions, then they will not decompose. * * * * The decomposition of peroxide of hydrogen into water and oxygen is retarded by some and accelerated by other substances. Platinum, silver oxide, and manganic dioxide, respectively, promote, whilst acids prevent the decomposition. Platinum possesses a great attraction for oxygen, its powder absorbs more than two hundred times its volume of the gas. This attraction is also exerted towards oxygen which is in chemical combination.
>
> If now a piece of platinum is placed in peroxide of hydrogen, the molecules of the latter will place themselves in such a position of the surface of the platinum, that one oxygen atom of the peroxide is turned towards the platinum and as near to it as possible. The peroxide is polarized. But this has the effect also of bringing the oxygen atoms of different molecules of peroxide in such close proximity on the surface of the metal that they can combine to form common oxygen, the decomposition of the peroxide into water and oxygen and development of energy being the consequence. The action of the platinum places the molecules of the peroxide in *the position of reaction* towards each other. The actions of silver oxide and of black oxide of manganese are similar.

There are a couple of interesting cases of what appears to be poisoning of the catalytic agent; but the data are not sufficient to warrant very definite conclusions.[89] Phosgene reacts with water to give carbon dioxide and hydrochloric acid,

$$COCl_2 + H_2O = CO_2 + 2HCl.$$

So far as is known, this reaction is not reversible and it actually runs to an end in presence of an excess of water. In presence of concentrated hydrochloric acid, however, the rate of hydrolysis is practically negligible. The most plausible way of accounting for this is by assuming that water and phosgene do not react by themselves and that the reaction takes place solely in contact with the walls of the containing vessel. When these are coated with a film of hydrochloric acid of sufficient concentration, practically no phosgene is adsorbed and no reaction takes place. The hydrolysis should be studied with different concentrations of hydrochloric acid and with a varying ratio of wall surface to mass of solution. If this explanation is correct, it may account for the rather surprising stability of a phosgene cloud in the damp atmosphere of Flanders, there being no catalytic agent in the cloud to cause the decomposition of the phosgene. On this basis, a cloud consisting of a mixture of hydrochloric acid and phosgene would be even more stable; but of course this would introduce serious complications in regard to loading.

Trimethylchloroformate, $ClCO_2CCl_3$, or superpalite as it is called, decomposes to carbon tetrachloride and carbon dioxide in presence of alumina,

$$ClCO_2CCl_3 = CO_2 + CCl_4,$$

and to phosgene in presence of ferric oxide,

$$ClCO_2CCl_3 = 2COCl_2.$$

The reverse reaction has never been made to take place to any measurable extent. During the war some superpalite and ferric oxide were placed in a glass tube connected with a closed manometer. There was rapid decomposition at first, as shown by the increase in pressure; but, before long, the reaction apparently came to an end. On raising the temperature, the reaction went a little farther and did not reverse when the temperature was brought back to its original value. Since this experiment was not repeated there may be some error in it and the facts may not be as stated; but it looks as though the ferric oxide was poisoned and as though the change of temperature modified the adsorption so that more superpalite came in contact with the catalytic agent and was decomposed. If this is the true explanation, it suggests one interesting set of experiments. When ethyl butyrate and water are treated with a small amount of lipase,[90] the decomposition proceeds only a little way, owing to the poisoning of the enzyme by the reaction products.[91] It seems probable that with an oscillating temperature it might be possible to carry the reaction much farther with the same amount of enzyme.

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[88] *J. Chem. Soc.*, **53** (1888), 327; Cf. Hüfner, *J. prakt. Chem.*, [2] **10** (1874), 385; Raschig, *Z. angew. Chem.*, **1906**, 1078; Gillet, *Bull. soc. chim. Belg.*, **30** (1921), 138.

[89] Bancroft, *Trans. Am. Electrochem. Soc.*, **36** (1919), 140.

[90] Kastle and Loevenhart, *Am. Chem. J.*, **24** (1900), 491.

[91] Bancroft, *J. Phys. Chem.*, **22** (1918), 40.

(To be continued)

Isotopes

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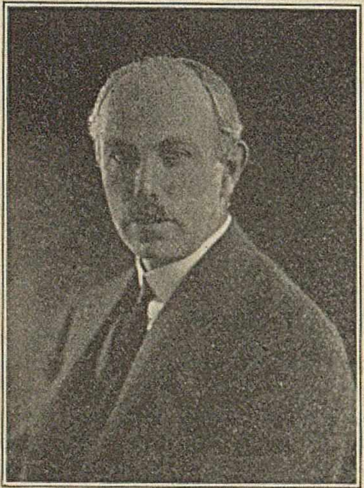
The attention of chemists is called to the remarkable developments which are being made in our knowledge of the fundamental structure of matter and energy. The work of the Cavendish Laboratory in the last few years leaves but little doubt that our complicated system of elements is in reality built up from two simple units, the electron and the proton, the latter being the real unit of mass, the atom of positive electricity, and identical with the nucleus of the hydrogen atom. The work of Rutherford and his associates has shown that artificial radioactivity may be stimulated in the ordinary elements. Hydrogen has been expelled by alpha particles, which are but positively charged helium atoms traveling at a velocity imparted by 6,000,000 volts, from the atoms of nitrogen, boron, fluorine, sodium, aluminium, and phosphorus. In many cases this expulsion is accompanied by an evolution of energy, in the case of aluminium of 40 per cent more than that possessed by the helium projectile.

Lately, Dr. F. W. Aston, who has been delivering a course of lectures at the Franklin Institute, has found that most of the elements of fractional atomic weights are really composed of isotopes whose atomic weights are integers to an accuracy of one part in a thousand. At the same time he has found another possible source of interatomic energy. His work is a masterpiece of ingenuity and skilled technic, and is an illustration of the value of tireless perseverance in searching for the meaning of apparently trivial deviations of numerical results from one another. A synopsis of a lecture by Dr. Aston before the local branches of the American Institute of Electrical Engineers and the American Chemical Society at Schenectady on April 7, 1922, follows:

> In 1803 John Dalton gave to chemistry what is probably one of the greatest generalizations in its history, the atomic theory. All of his five postulates have since stood the test of over a century of active and unremitting investigation except the one which states that "atoms of the same element are similar to one another and equal in weight."
>
> No direct method was available for testing this hypothesis until 1910, when Sir J. J. Thomson showed that sharply defined parabolic streaks were obtained on a photographic plate when beams of positively charged ions were deflected by means of magnetic and electrostatic fields. This proved that the ratio of the charge of electricity to the mass of the particle was constant for all the ions forming the parabola, and since the charge was known to be a definite unit, that the masses of the individual atoms were approximately the same. But the apparatus was not sufficiently accurate to detect small variations in weight.

However, indirect evidence that there might be different atoms of the same element was forthcoming from the work of Sir Ernest Rutherford and others. Investigations of the transformations undergone by different radioactive families showed that lead could be formed in several ways. Each kind of lead was found to be identical chemically with the others, but the atomic weights calculated from that of the original substance by subtraction of the masses of the alpha particles emitted in the radioactive transformations indicated that the atomic weights must be different. Thus lead from the uranium series should have an atomic weight of 206, lead from thorium 208, while ordinary lead has a weight of 207.2. Careful investigation of lead from various radioactive minerals by Richards, Soddy, Hönigschmidt, and others showed differences in their atomic weights which by far exceeded the possible experimental error.


F. W. Aston

These substances which have different atomic weights but the same position in the periodic table were called "isotopes" by Professor Soddy.

Moseley's epoch-making discovery has shown us that the chemical properties of the elements have nothing whatever to do with their atomic weights but do depend on a much more fundamental factor, the atomic number, or the number of positive charges on the nucleus of the atom. Isotopes may be shortly defined, therefore, as elements having the same atomic number but different atomic weights.

The first indication that the nonradioactive elements might also have isotopes was given by Sir J. J. Thomson, when he announced that when neon was analyzed by the positive ray method, two parabolas were indicated, corresponding to the atomic weights 20 and 22. In 1913 Aston succeeded in fractionating these two gases by diffusion through pipe clay and obtained two parts differing by 0.7 per cent in density. This result is in agreement with the separation theoretically possible, as determined from later and more accurate work.

After the war Dr. Aston continued this investigation with the idea of making the method of analysis so accurate that the atomic weights of the gases in question would be definitely settled.

In order to do this he radically modified Thomson's positive ray apparatus, so that atomic masses can now be determined to an accuracy of one part in a thousand.

By the application of specially designed magnetic and electrostatic fields to positively charged ions emerging from a narrow slit in the cathode of an electrical discharge tube, he is able to deflect beams of ions which come to a focus on a photographic plate. Each line is produced only by charged atoms having exactly the same atomic weight, and the lines due to different atoms are separated by distances proportional to their masses. Thus a mixture of atoms can be separated into rays of particles having equal mass in an analogous way to the resolution of ordinary light by the spectrograph into its components of different wave lengths. On account of this similarity the instrument has been called a positive ray spectrograph, and the spectrum produced, a mass spectrum.

When neon was subjected to analysis in this way it was found that lines corresponding to atomic weights of exactly 20 and 22 made their appearance. The latter line was much fainter than the former, as it should be, since only 10 per cent of the heavier isotope is required to make the mean atomic weight of ordinary neon 20.2.

Similar analyses were then made of as many of the elements as possible, with the result that many of our supposedly simple elements have been resolved into two or more isotopes. The following table summarizes the results thus far obtained:

Element	Atomic Number	Atomic Weight	Minimum Number of Isotopes	Masses of Isotopes in Order of Their Intensity
H	1	1.008	1	1.008
He	2	3.99	1	4.0
Li	3	6.94	2	7, 6
B	5	10.9	2	11, 10
C	6	12.0	1	12
N	7	14.01	1	14
O	8	16	1	16
F	9	19	1	19
Ne	10	20.2	2	20, 22, 21?
Na	11	23	1	23
Mg	12	24.32	3	24, 25, 26
Si	14	28.3	2	28, 29, 30?
P	15	31.04	1	31
S	16	32.06	1	32
Cl	17	35.46	2	35, 37, 39?
A	18	39.88	2	40, 36
K	19	39.1	2	39, 41
Ca	20	40.09	1	40 (39, 40, 41)
Ni	28	58.68	2	58, 60
Zn	30	65.4	3	64, 66, 68, (70)
As	33	74.96	1	75
Br	35	79.92	2	79, 81
Kr	36	82.92	6	84, 86, 82, 83, 80, 78
Rb	37	85.45	2	85, 87
I	53	126.92	1	127
Xe	54	130.20	5 (7?)	129, 132, 131, 134 136, 128? 130?
Cs	55	132.81	1	133
Hg	80	200.6	6	197–200, 202, 204

The most significant result of these measurements is that, with the exception of hydrogen, the weights of all the elements measured are whole numbers to an accuracy of 0.1 per cent. Also the relative positions of potassium and argon, nickel and cobalt, are reconciled with the order of increasing mass in the periodic table.

This immediately revives the original hypothesis of Prout, suggested in 1815, that atoms were themselves built up from particles of Protyle, which he endeavored to identify with hydrogen. The modern development of this idea is that the ultimate particles of matter are composed of atoms of positive electricity, or protons, and the atoms of negative electricity, or electrons. The proton appears to be the real unit of mass and is identical with the nucleus of the hydrogen atom.

Since isotopes are identical in their chemical behavior, physical methods only are available for their separation. Neon has been partly separated into its constituents by Aston; chlorine, by Harkins, and mercury, by Brönsted and Hevesy.

Since hydrogen has an atomic weight greater than unity, one would naturally expect that when four atoms of hydrogen combine to form an atom of helium the resulting atomic weight would be 4.032 instead of exactly 4.00. When the positive and negative charges of the hydrogen, which are relatively very far apart, are compressed into the helium nucleus, from the electromagnetic theory of mass, a loss of mass due to "packing" should occur. But when mass is annihilated, energy should appear, and assuming the loss of mass as measured, it may be calculated that if the hydrogen in 9 cc. of water were transformed to helium 200,000 kw. hrs. would be evolved. Dr. Eddington believes that this answers the riddle of why the sun keeps hot, since if 10 per cent of the hydrogen present in the sun condenses to form helium, enough energy would be supplied to maintain the present temperature for 1,000,000,000 years.

Chemical Plant Equipment Manufacturers

The organization committee of the Association of Chemical Plant Equipment Manufacturers will call a meeting in New York for the purpose of completing the organization of this Association. The following program has been arranged:

On Tuesday, May 9, at 8 o'clock, the members of the Association will be addressed by Dr. Julius Klein, of the U. S. Department of Commerce, and Mr. E. W. McCullagh, Manager of the Fabricated Production Department of the U. S. Chamber of Commerce.

On Wednesday morning, May 10, at 10 o'clock, the organization meeting will be held and the formal organization will be completed. At 2:00 P.M., the members of the Association will be addressed by Mr. Charles Roth, of the Chemical Exposition Show, Mr. Campbell, of the Boston Textile Show, Mr. Reeves of the New York Automobile Show, and Mr. Ebertt, of the Ice Cream Supply Dealers Association.

These meetings will be held at the Chemists' Club, 52 E. 41st St., New York City.

The Atlas Valve Company of Newark, N. J., has announced the production of an automatic low water shut-off valve made especially for application to gas fired steam boilers.

SCIENTIFIC SOCIETIES

Calendar of Meetings

American Oil Chemists' Society—13th Annual Meeting, New Orleans, La., May 8 and 9, 1922.

American Zinc Institute—St. Louis, Mo., May 8 and 9, 1922.

Institute of Metals Division of A. I. M. E.—Rochester, N. Y., June 5 to 9, 1922.

National Fertilizer Association—29th Annual Convention, White Sulphur Springs, W. Va., week of June 12, 1922.

American Institute of Chemical Engineers—14th Semiannual Meeting, Niagara Falls, Ontario, June 19 to 22, 1922.

American Leather Chemists Association—19th Annual Meeting, Ontario, Canada, June 21 to 23, 1922.

Alpha Chi Sigma Fraternity—7th Biennial Conclave, St. Louis, Mo., June 22 to 24, 1922.

American Society of Testing Materials—25th Annual Meeting, Atlantic City, N. J., June 26 to July 1, 1922.

Sixty-third Meeting, American Chemical Society, Birmingham, Alabama, April 3 to 7, 1922

Program of Papers

GENERAL MEETING

Hon. Nathan L. Miller, Lieutenant Governor of Alabama. Address of Welcome.

Edgar F. Smith, President, American Chemical Society. Response.

Carlile P. Winslow, Director, U. S. Forest Products Laboratory. The Development of the Forest Products Industry in the South.

William H. Stone, Associate Editor, *Manufacturers Record*. The Remarkable Development of the South and Its Relations to the American Chemical Industry.

Theodore Swann. The Manufacture of Phosphoric Acid in the Electric Furnace by the Condensation and Electrical Precipitation Method.

Van H. Manning. The Pioneer's Field in Petroleum Research.

Charles L. Reese. Informational Needs in Science and Technology.

W. C. Geer. Recent Developments of the Chemistry of Rubber.

W. D. Bigelow. Some Research Problems in the Canning Industry.

Francis P. Venable. Chemistry in the Old South and the New.

PUBLIC MEETING

Marston Taylor Bogert, Past President, American Chemical Society. The Flower and the Organic Chemist. Perfumes—Natural and Synthetic.

AGRICULTURAL AND FOOD CHEMISTRY DIVISION

T. J. Bryan, *Chairman* C. S. Brinton, *Secretary*

1. Benjamin R. Jacobs. Composition, Grade and Baking Qualities of Self-Rising Flours.
2. Juanita E. Darrah. Bleached and Self-Rising Flours.
3. Juanita E. Darrah. Composition and Nutritive Value of Yeast Grown in Vitamin-Free Media.
4. Juanita E. Darrah. New Sources of Water-Soluble C and Fat-Soluble A in the Southeast.
5. Edward Gudeman. Foods, Facts, Fancies, and Follies.
6. Edward F. Kohman. The Determination of Hydrogen Sulfide Evolved by Foods when Cooked at Various Temperatures.
7. C. S. Robinson. Studies of the Availability of Organic Nitrogenous Compounds—II. (By title.)
8. R. O. E. Davis. The Interpretation of Mechanical Analysis of Soils as Affected by Soil Colloids.
9. J. W. Sale and J. B. Wilson. Determination of Methyl Anthranilate.
10. J. B. Wilson and J. W. Sale. Determination of Methanol.
11. Edgar T. Wherry. Relations between the Active Acidity and the Lime Requirements of Soils.
12. M. F. Showalter and R. H. Carr. Characteristic Proteins in High and Low Protein Corn.
13. E. G. Mahin and R. H. Carr. Errors in the Determination of Fat in Cream.
14. William H. Ross, C. B. Durgin and R. M. Jones. The Commercial Purification of Phosphoric Acid by Crystallization.
15. E. R. Miller. Do Velvet Beans Contain Vitamin B?
16. B. B. Ross. The Occurrence and Composition of Some Alabama Phosphates.
17. H. H. King and M. C. Sewell. The Mineral Requirements for the Nutrition of Wheat during the Seedling Phase. (Lantern.)
18. E. H. S. Bailey. A Dietary Study of Some State Institutions.
19. Floyd W. Robison. Studies on the Electropure Process of Treating Milk. (Lantern.)
20. J. S. McHargue. The Role of Manganese in Plants. (Lantern.)
21. W. O. Robertson. The Absorption of Water by Soil Colloids.

BIOLOGICAL CHEMISTRY

Howard B. Lewis, *Chairman* J. S. Hughes, *Secretary*

1. J. C. Swenarton and E. Emmet Reid. Higher Alcohols Formed in the Fermentation of Sugar.
2. James F. Couch. The Toxic Constituent of Greasewood (*Sarcobatus vermiculatus*).
3. C. L. Hare. Influence of Breeding upon Oil and Protein Content of Cottonseed.
4. Jack Montgomery. The Iodine Absorption of Urine.
5. E. R. Miller. Influence of Sodium Chloride upon Animal Excretion.
6. Atherton Seidell. Further Experiments on the Isolation of Vitamin.
7. C. H. Hunt and A. R. Winter. Cow's Milk *vs.* Goat's Milk as a Source of Vitamin C. (Lantern.)
8. J. S. Hughes and H. B. Winchester. Results Obtained by Feeding Breeding Gilts a Ration Low in Fat-Soluble Vitamin. (Lantern.)
9. J. S. Hughes, L. D. Bushnell and L. F. Payne. The Influence of Vitamin Content of a Feed on the Immunity to Roop. (Lantern.)
10. Harper F. Zoller. The Detection and Estimation of Inorganic Activators in Commercial Rennin and Pepsin Preparations.
11. Harper F. Zoller. A Laboratory Disinfectant to Displace Mercuric Chloride Solutions.
12. I. K. Phelps and J. E. Basch. The Decomposition of Food by *Bacillus botulinus*.
13. Max Kahn. The Feeding of Non-Ketogenic Odd-Carbon Fats to Diabetic Patients. (By title.)
14. Arno Viehoever and Ruth G. Capen. A New Source of Santonin.
15. Victor E. Levine. A New Method for the Colorimetric Determination of Peroxidase.
16. Victor E. Levine. A Simple Method for Differentiating Boiled or Pasteurized Milk from Unboiled or Unpasteurized Milk.
17. Victor E. Levine. Selenium Compounds as Biochemical Reagents.
18. Victor E. Levine and Arthur C. Antony. The Catalytic Properties of the Metals Occurring in Respiratory Pigments.

CELLULOSE CHEMISTRY SECTION

Harold Hibbert, *Chairman* G. J. Esselen, Jr., *Secretary*

1. Report of the Standard Cellulose Committee.
2. Report of the Analytical Methods Committee.
3. Report of the Viscosity Measurement Committee.
4. E. C. Sherrard and A. W. Froehlke. The Effect of Concentrated Hydrochloric Acid on Different Celluloses.
5. E. C. Sherrard and W. H. Gauger. The Effect of Salts upon the Acid Hydrolysis of Wood.
6. E. C. Sherrard and C. F. Suhn. Sugar Formation in a Sulfite Digester.
7. E. C. Sherrard. Ethyl Alcohol from Western Larch.
8. E. C. Sherrard and G. W. Blanco. Some of the Products Obtained in the Hydrolysis of White Spruce Wood with Dilute Sulfuric Acid under Steam Pressure.
9. L. F. Hawley and S. S. Aiyar. The Distribution of Methoxyl in the Products of Wood Distillation.
10. G. J. Ritter and L. C. Fleck. The Chemistry of Wood—V.
11. S. A. Mahood and D. E. Cable. The Chemistry of Wood. IV—The Analysis of Western White Pine and Eucalyptus.
12. S. A. Mahood. Some Observations on the Determination of Cellulose in Woods—II.
13. W. O. Mitscherling. Preparation of a "Standard Cellulose."
14. Harold Hibbert and Harold S. Hill. Synthesis of Derivatives Relating to Polysaccharides.
15. Harold Hibbert and John A. Timm. Synthesis and Properties of Cyclic Acetal Derivatives.
16. Harold Hibbert. Constitution of Sedoheptose Anhydride and Its Relation to Cellulose.

17. Symposium. The Action of Alkali and Acid on Cellulose, Wood and Waste Cellulosic Material with Special Reference to the Production of Cheap Cattle Foods.
18. Joint Symposium with Division of Organic Chemistry. Recent Work on the Constitution of Starch and Cellulose.

CHEMICAL EDUCATION SECTION

Edgar F. Smith, *Chairman* Neil E. Gordon, *Secretary*

An Ideal First Year Course in Chemistry

1. William McPherson. First Year College Chemistry.
2. Wilhelm Segerblom. High School Chemistry.
3. Miss Minnie B. Fisher. First Year Chemistry for Women.
4. Eugene C. Bingham. Teaching of the Metric System in First Year Chemistry.
5. F. P. Venable. Methods for Presenting First Year Chemistry.
6. Neil E. Gordon. Teaching First Year Chemistry by the Project Method.

Chemical Engineering Education

7. W. K. Lewis and R. T. Haslam. Studying Chemical Engineering by the Unit-Operation Method.
8. J. L. Daniel. Standardization of Courses in Quantitative Analysis for Students in Chemical Engineering.
9. R. H. McKee. Discussion of Committee's Report on Chemical Engineering Education.
10. L. J. Desha. Correlation of Engineering Thermodynamics with Chemical Thermodynamics.
11. C. S. Williamson, Jr. Importance and Time Given for Courses in Economics and Industrial Management in Chemical Engineering Training.
12. Graham Edgar. Distribution of Time between "Pure" and "Applied" Science.

Round-table discussion.

13. Marston Taylor Bogert. Recent Progress at Columbia University.
14. J. N. Swan. Some Laboratory Helpers.
15. Charles W. Cuno. A Chart of the Synthetic Intermediates.
16. H. A. Webb. Standard Test in Science, especially Chemistry.
17. W. F. Hand. Training for Agricultural Chemistry.
18. Jack P. Montgomery. Unified Chemistry Courses.
19. Edward G. Mahin. Science or Athletics?

DYE CHEMISTRY DIVISION

William J. Hale, *Chairman* R. Norris Shreve, *Secretary*

1. Herbert L. Haller. The Preparation of Phenylglycine-*o*-carboxylic Acid. I—From Anthranilic Acid and Monochloroacetic Acid. (Lantern.)
2. Max Phillips. On the Preparation of 7,7′-Di(-hydroxy-isopropyl)-indigo.
3. S. Palkin. A New Method for the Preparation of Dicyanine and Related Dyes. (By title.)
4. C. R. DeLong and W. N. Watson. The Necessity for Reclassification and Standardization of Dyes.
5. W. R. Waldron and E. Emmet Reid. The Influence of Sulfur on Colors of Azo Dyes.
6. Marston Taylor Bogert and Martin Meyer. Experiments with Dehydrothio-*p*-toluidine and Related Compounds.
7. Jules Bebie. Uses of *p*-Toluene-sulfonyl Chloride in the Manufacture of Dyes and Intermediates.
8. Andrew J. Leddy. The Method of Determining the Class to Which Each Dye Belongs.
9. Andrew J. Leddy. The Function of Assistants Used in Dyeing Cotton.
10. Walter C. Holmes. The Application of the Direct Dyes in Coloring Paper.
11. R. E. Rose. The Functions of the Dye Testing Laboratory.
12. Henry R. Lee and D. O. Jones. The Analysis of β-Naphthylamine.

HISTORY OF CHEMISTRY SECTION

C. A. Browne, *Chairman* Lyman C. Newell, *Secretary*

1. Edgar F. Smith. Dr. Thomas Cooper—A Pioneer American Chemist.
2. C. A. Browne. Several Early References Pertaining to Chemical Warfare.
3. George L. Coyle. The Chemical and Scientific Achievements of Father Athanasius Kircher, S. J.
4. Ralph H. McKee. Some Photographic Reminiscences of the Priestley Centennial of 1874.
5. John N. Swan. A Book and a Battery.
6. J. A. Gunton. An Early Type of Chemical Slide-Rule.
7. William McPherson. Reminiscences of Italian Chemists.

Symposium on the History of Early Chemical Industries in America, More Particularly of Those in the South

8. C. A. Browne. A Few Sources of Information upon Early Chemistry and Chemical Industries in America.
9. B. B. Ross. Some Facts Relating to Early Chemists and Chemical Industries in Alabama.
10. Elton R. Darling. History of the Early Salt Industry of the Ohio River and Kanawha Valley.
11. Eugene A. Smith. Some Early Southern Chemists and Their Work.

INDUSTRIAL AND ENGINEERING CHEMISTRY

W. K. Lewis, *Chairman* E. M. Billings, *Acting Secretary*

I—Symposium on Distillation

W. A. Peters, Jr., *Chairman*

1. W. A. Peters, Jr. Efficiency and Capacity of Fractionating Columns. (Lantern.)
2. Clark S. Robinson. The Plate Efficiency of a Continuous Alcohol Still.
3. W. K. Lewis and Clark S. Robinson. The Simple Distillation of Hydrocarbon Mixtures.
4. S. S. Heide. Benzene Purification.
5. C. A. Lambert. Wood Turpentine.
6. W. K. Lewis and Harold C. Weber. The Calculation of the Heats of Vaporization of Various Liquids, First, by Means of the Hildebrand Function; Second, from Vapor Pressure Curves.
7. J. W. Bodman. Present Practice of Dynamite and Chemically Pure Glycerol Distillation.
8. McGarvey Cline. Turpentine Distillation.

II—General Papers

9. A. C. Fieldner and G. W. Jones. Carburetor Adjustment by Gas Analysis. (Lantern.)
10. G. J. Fink. Investigations of Whitewashes and Aqueous Lime Paints. (Lantern.)
11. R. Norris Shreve. Can We Afford to Make Potash in America?
12. L. F. Hawley. Discontinuous Extraction Processes.
13. S. W. Parr. The Classification of Coal.
14. A. C. Fieldner, W. A. Selvig and W. L. Parker. A Comparison of the Standard Gas Furnace and Micropyrometer Methods for Determining the Fusibility of Coal Ash. (Lantern.)
15. S. W. Parr and C. N. Davidson. The Calorific Value of American Woods.
16. S. P. Kinney and G. St. J. Perrott. The Shatter and Friability Tests for Metallurgical Coke.
17. Harold J. Rose. Determination of True Specific Gravity of Coke.
18. G. St. J. Perrott and H. W. Clark. Smokeless Fuel for Salt Lake City.
19. S. W. Parr. The Ultimate Analysis of Coal by Utilization of Sodium Peroxide Fusions.
20. W. D. Collins. The Value of Brands to Buyers.
21. Arthur L. Davis. Acetone, Butanol, Ethanol and Gas from the Butyric Fermentation of Corn.
22. A. F. Thal. Crystallization in Transparent Soap. (By title.)
23. Lloyd Logan. The Control of Industrial Processes by Light Sensitive Means. (By title.)

ORGANIC CHEMISTRY DIVISION

H. T. Clarke, *Chairman* Frank C. Whitmore, *Secretary*

1. M. C. Sneed and J. Louis Maynard. Preparation of Methylmercuric Acetate and Methylmercuric Hydroxide.
2. Henry C. Howard, Jr., and J. Louis Maynard. An Electrolytic Method for the Preparation of Mercury Dimethyl from Methylmercuric Hydroxide.
3. William A. Noyes and H. M. Chiles. The Asymmetry of Diazodiethyl Glutarate.
4. L. Charles Raiford and Liang Yi Ho. Further Observations on the Nitration of Halogenated Phenols.
5. Marston Taylor Bogert and Y. G. Chen. New Organic Selenium Compounds.
6. Marston Taylor Bogert and E. Abrahamson. The Synthesis of a Thiazole Analog of Cinchophen (Atophan).
7. Edward C. Franklin. Hydrocyanic Acid: An Ammono Carbonous Acid and an Ammono Formaldehyde.
8. Henry Gilman and Charles H. Meyers. A Study of the Optimum Condition for the Formation of the Grignard Reagent.
9. Henry Gilman and Harry L. Morris. The Reaction between Thionyl Aniline and the Grignard Reagent.
10. W. Lee Lewis and R. S. Bly. Arsenated Heterocyclic Compounds Prepared from 3,4-Diamino-phenylarsonic Acid.
11. W. Lee Lewis and H. W. Stiegler. Derivatives of the β-Chlorovinyl Arsines.
12. Francis D. Dodge. Chemical and Crystallographic Notes on the Acid Phthalates.
13. Francis D. Dodge. The Occurrence of Formic Acid in Essential Oils.
14. De Witt Neighbors, S. M. Clark. J. E. Miller, A. L. Foster and J. R. Bailey. Catalytic Reduction of the C-N Complex.
15. Harold Hibbert and Harold S. Hill. The Preparation of Mono- and Parabromoacetaldehyde and Their Application to Synthetic Work in Cellulose Chemistry.

16. Harold Hibbert and Roland R. Reed. The Electrolytic Reduction of Crotonaldehyde.
17. C. S. Adams and C. E. Boord. Absorption Spectra of Phenylazophenol and Its Derivatives in the Visible Region. (Lantern.)
18. L. B. Sebrell and C. E. Boord. Preparation and Properties of 1-Mercaptobenzothiazole and Its Derivatives. (Lantern.)
19. C. S. Palmer and Roger Adams. The Condensation of Primary Aromatic Arsines with Aldehydes.
20. Edmund Burrus Middleton and Frank C. Whitmore. Organo-mercury Compounds Formed from Salicylaldehyde and Its Nitro Derivatives.
21. Frank C. Whitmore and Louis Ehrenfeld. Organo-mercury Compounds Formed from Benzenesulfonic and Benzylsulfonic Acids. A Preliminary Report.
22. Jack P. Montgomery. Mass Action in the Preparation of Compounds of Urea with Acids and Salts.
23. T. B. Aldrich and Julia E. Blanner. Mononitro Derivatives of the Benzoic Acid Esters of the Trihalogen Tertiary Butyl Alcohols.
24. E. C. Kendall and A. E. Osterberg. Some Reaction Products of Malonic Ester and Cyclohexane Derivatives.
25. A. B. Brown and E. Emmet Reid. The Alkylation of Aniline.
26. A. B. Brown and E. Emmet Reid. The Amination of Alcohols.
27. T. M. Berry and E. Emmet Reid. The Alkylation of Benzene.
28. Henry Gilman and Chester E. Adams. Ditolyl-ketene.
29. F. B. Flick, H. M. Crawford, R. Hoyle and H. Gilman. The Effect of an *iso* Grouping on the Melting and Boiling Points of Organic Compounds.
30. Henry Gilman and Russell M. Pickens. Physiological Action and Chemical Constitution: The Replacement of the Benzoyl by Related Acyl Groups.
31. W. Lee Lewis and H. C. Cheetham. Arsenated Benzophenone and Its Derivatives—II.
32. W. Lee Lewis and C. S. Hamilton. Arsenated Benzanilide and Its Derivatives.
33. W. L. Evans, C. A. Buehler and R. A. Crawford. The Oxidation of *d*-Glucose, *d*-Mannose and *d*-Galactose with Alkaline Permanganate.
34. Arthur J. Hill and Dewitt T. Keach. Application of Chloro Ethers for the Preparation of Some New Derivatives of Diethyl Malonate and Barbituric Acid.

PETROLEUM CHEMISTRY SECTION

T. G. Delbridge, *Chairman* W. A. Gruse, *Secretary*

1. A. P. Bjerregaard. Volume Changes in Petroleum Products.
2. C. K. Francis and H. T. Bennett. The Surface Tension of Petroleum.
3. W. H. Herschel. The Change in Viscosity of Oils with Temperature. (Lantern.)
4. W. H. Fulweiler and C. W. Jordan. Some Notes on the Determination of the Absolute Viscosity of Petroleum Oils.
5. Thomas Midgley, Jr., and T. A. Boyd. The Compression Values of Blended Motor Fuels.
6. C. J. Rodman. The Catalytic Oxidation of Insulating Oils.
7. R. R. Matthews and P. A. Crosby. Corrosion of Petroleum Refining Equipment.
8. F. E. Hosmer and F. M. Seibert. Recent Developments in the Methods for Extraction of Gasoline from Natural Gas.
9. Edwin DeBarr and F. W. Padgett. Petroleum Education.
10. Conference on the Promotion of Research on Petroleum.
11. C. E. Waters. Sulfur Compounds and the Oxidation of Petroleum Oils. (By title.)

PHYSICAL AND INORGANIC CHEMISTRY

S. E. Sheppard, *Chairman* R. E. Wilson, *Secretary*

1. Robert B. Sosman. Theory of the Structure and Polymorphism of Silica. (Lantern.)
2. Hamilton P. Cady and Howard M. Elsey. A General Conception of Acids, Bases and Salts.
3. Edgar T. Wherry. Crystallography and Atomic Structure. (Lantern.)
4. A. S. Richardson, F. C. Vibrans and W. P. Bell. Equilibrium in the Reduction of Iron Oxides and in the Oxidation of Iron by Steam. (Lantern.)
5. Stewart J. Lloyd. Solubility Measurements on Sulfur Dioxide.
6. Graham Edgar and William H. Schuyler. Esterification Equilibria in the Gaseous Phase.
7. N. E. Gordon and E. Emmet Reid. Partition Ratios and Solubility Numbers.
8. William A. Noyes and Thomas A. Wilson. The Amphoteric Ionization of Hypochlorous Acid.
9. W. V. Evans and Louise Otis. The Ionization of Butyl Mercury Hydroxide.
10. Edward C. Franklin. Ammono Nitric Acid.
11. Eugene C. Bingham and H. L. Young. The Drainage Error in Viscosity Measurements of Viscous Materials by the Capillary Tube Method.
12. Robert H. Bogue. Hydrogen-Ion Concentration and the Properties of the Emulsoid Colloids.
13. S. E. Sheppard and S. S. Sweet. The Elasticity of Ash-Free Gelatin Jellies. (Lantern.)
14. Harry B. Weiser. The Formation of Inorganic Jellies: General Theory.
15. H. H. King and R. W. Wampler. The Adsorption and Orientation of Molecules of Dibasic Organic Acids and Their Ethereal Salts in Liquid-Vapor Interfaces. (Lantern.)
16. B. S. Hopkins and F. H. Driggs. Atomic Weight of Lanthanum.
17. E. B. Starkey and Neil E. Gordon. Thermoregulator. (Lantern.)
18. Jack P. Montgomery. The Concentrations of Alkali Halide Solutions, of the Order of 0.001 *N*, Most Favorable to Adsorption by Barium Sulfate.
19. L. J. Curtman and D. Hart. The Transposition of Insoluble Oxalates by Sodium Carbonate Solution.
20. Louis J. Curtman and N. H. Hecht. A New Method for the Volumetric Determination of Iron.
21. Louis J. Curtman. Two New Pieces of Apparatus for Use in Analytical Work.
22. Graham Edgar and R. B. Purdum. Rapid Electrolysis without Mechanical Stirring.
23. Eugene C. Bingham and Herbert D. Bruce. The Relation of Yield Value and Mobility to the So-called Painting Consistency of Paints.
24. Harry B. Weiser. Hydrous Oxide. IV—Hydrous Stannic Oxide.
25. S. E. Sheppard and S. S. Sweet. The Interfacial Tension between Toluene and Ash-Free Gelatin Solution. (Lantern.)
26. James M. Bell. The Nitration of Toluene.

RUBBER CHEMISTRY DIVISION

C. W. Bedford, *Chairman* Arnold H. Smith, *Secretary*

1. R. P. Dinsmore. Internal Mixers.
2. Ira Williams. The Thermal Properties of Rubber and Rubber Pigments.
3. H. W. Greider. Physical Properties of Rubber Compounded with Light Magnesium Carbonate. (Lantern.)
4. Norman A. Shepard and Stanley Krall. The Relation between Chemical and Physical State of Cure of Rubber Vulcanized in the Presence of Certain Organic Accelerators. (Lantern.)
5. W. B. Wiegand. Physical Testing Graphs. (Lantern.)
6. Rubber Division Methods for Rubber Analysis Report of Committee, and Discussion.
7. Organic Accelerators. Symposium. Specification Standards and Testing, including Both Chemical and Physical Tests in Compounds.

SUGAR CHEMISTRY DIVISION

S. J. Osborn, *Chairman* Frederick Bates, *Secretary*

1. C. A. Browne. The Moisture Absorptive Power of Different Sugars and Carbohydrates.
2. W. D. Horne. Sugar Purity Determinations.
3. C. E. G. Porst and M. Moskowitz. Plastometer Tests on Alkaline Thin Boiling Cornstarches.
4. H. T. Ruff and J. R. Withrow. The Determination of Gums in Raw Sugars.
5. O. A. Sjostrom. The Determination of the pH Value of Commercial Glucose as a Substitute for the Candy Test.
6. B. B. Ross. Some Notes on the Determination of Reducing Sugars.
7. W. P. Valentine. An Improved Precision Refractometer for the Sugar Industry.
8. M. H. Wiley. The Observance of Mutarotation in the Polarization of Raw Cane Sugar.
9. F. W. Zerban. Note on the Color Range of Cane Sirups and Molasses.
10. C. E. Coates. Manufacture of Plantation Standard Granulated Sugar with and without Activated Char.
11. P. M. Horton. The Decolorizing Power of Bone Char. (Preliminary Report.)
12. W. D. Horne. Color and Ash Absorption by Boneblack and Decolorizing Carbons.
13. J. F. Brewster and W. G. Raines, Jr. Control of Reaction in Sugarhouse (and Refinery) Liquors. (Lantern.)
14. J. F. Brewster and W. G. Raines, Jr. The Precipitate Formed in Sugarhouse Sirups. (Lantern.)
15. H. H. Peters and F. P. Phelps. Modifications in the Use and Application of the Hess-Ives Tint Photometer. (Lantern.)
16. W. B. Newkirk and H. H. Peters. Color Values of High-Grade Sugars. (Lantern.)
17. E. P. Clark. Note on a Laboratory Vacuum Still. (Lantern.)
18. R. S. Black. The Preparation of Adonitol.

WATER, SEWAGE AND SANITATION DIVISION

A. M. Buswell, *Chairman* W. W. Skinner, *Secretary*

1. Edward Bartow, M. E. Flentje and W. U. Gallaher. The Effect of Temperature on the Rate of Reaction in Water Softening by the Lime-Soda Ash Method.
2. A. M. Buswell. Observations on the Mechanism of Iron Removal.

3. J. W. Sale. Specific Gravity of Mineral Waters by Calculation.
4. W. W. Skinner, C. H. Badger and J. W. Sale. Bottled Mineral Waters of Unusual Composition.
5. W. F. Monfort. Two Instances in Which Acute Troubles Were Explained by Means of the pH Determination.
6. W. D. Hatfield. Data on the Application of pH Value to the Operation of Filtration Plants.
7. A. M. Buswell. Formulation of Equilibria in the Coagulating Basin.
8. A. M. Buswell. Report of Committee on Standard Methods of Analysis.

Topic for Discussion: Specifications for Lime for Water Treatment.

The Chemical Exposition

The Eighth National Exposition of Chemical Industries will be held this year in the Grand Central Palace, New York, during the week of September 11 to 16, inclusive. It will follow immediately upon the Fall Meeting of the American Chemical Society. The early date will give college and university men an opportunity to see the exhibits before the beginning of the college year. There is much in this coming Exposition to interest university men. Each floor in the Exposition has exhibits of laboratory apparatus, and one floor has a considerable group of this type of equipment. Many new pieces of apparatus, new chemical compounds, and other material and instruments will be found here.

The interests for industrial chemistry in the Exposition are wide and varied: from raw materials in minerals, ores, manufacturing crudes or by-products, through the range of machinery, apparatus and equipment and instruments for control, precision, recording, gaging and measuring, and a thousand other items used in converting the raw materials into the finished products. The finished products themselves, whether they be organic, inorganic, solid, liquid, gaseous, or of any other form, are all to be there. Many new things upon which manufacturers were working when the war ended and which have been more leisurely perfected since will be shown for the first time. Industrial progress continually calls for greater advancement and perfection in manufacture, and each year sees many notable improvements upon the exhibits in the Exposition. Counting only these, the time of technical and business men is well spent in inquiring into the exhibits. One exhibitor, who for the past few years has been devoting time to the perfection of a new form of apparatus, said the other day that it is now when men have time to spare for consideration of these things that he expects a considerably larger and more interested attendance in his booth. "When the plants are idle as they are now, the most progressive companies are examining into our apparatus, and a remarkable thing is that we are making some installations in plants which are now closed, so that when they begin work they will be in better position than ever and have an advantage in taking this opportunity to prepare to reduce their costs for the future. I'm looking for many more such openings through our exhibit and with considerable enthusiasm for the entire Exposition."

The managers report that three full floors of the Grand Central Palace are already taken for the Exposition and a part of a fourth. They expect all space will be engaged before the opening date. Already, 303 exhibitors have contracted for space.

The Exposition will contain two interesting special sections: one upon the subject of fuel economy, where exhibits intended for the more efficient use of fuel, its combustion, distribution, or control will be made. The other will deal with shipping containers, including the container itself, whether of metal, wood, fiber, paper, glass or in cooperage products of slack and tight barrels, tanks and towers, and with machinery for packaging, labeling, handling, and conveying the packaged material and marking it ready for final shipment.

Work upon the program has not yet been actively undertaken but it may be expected to compare more than favorably with the high standards of the preceding Expositions. The management have returned to the Grand Central Palace with their offices, and all inquiries should be directed there.

Plan Now for Pittsburgh in September!

Convention dates, September 5 to 9, 1922

We are actively preparing for the coming of our guests, having special regard to arrangements for comfortable quarters at minimum cost, convenient and suitable meeting places, cordial welcome and interesting entertainment, excellent technical program and profitable excursions to glass works, enameling plants, iron and steel plants of all kinds, zinc and sulfuric acid plants, coal mines, and by-product coke plants.

Dormitory accommodation at a maximum rate of \$1.50 per day will be available for 350 men and 50 ladies. Hotel space will be ample if arranged for well in advance.

The great Music Hall of the Carnegie Institute has been placed at our disposal for the opening meeting and for the public meeting. We hope to combine registration and personal welcome before the opening meeting, Wednesday morning.

The meetings, except that of the Council, will be held in the neighborhood of the Carnegie Institute.

The ladies will be especially well entertained. Details will be announced later.

We hope that the attendance at the meeting will break all records.

James Otis Handy, *Chairman*

S. O. C. M. A. Officers

The Synthetic Organic Chemical Manufacturers Association of the United States held its first Annual Meeting at the Hotel Pennsylvania on Friday, March 31, 1922.

Officers for the ensuing year were elected as follows:

President: Chas. H. Herty
Vice Presidents:
  Dyestuff Section, C. N. Turner, Newport Chemical Works, Passaic, N. J.
  Intermediate Section, Chas. A. Meade, E. I. du Pont de Nemours & Co., Wilmington, Del.
  Pharmaceuticals Section, Herman Seydel, Seydel Mfg. Co., Jersey City, N. J.
  Fine Organic Chemicals Section, P. Schleussner, Roessler & Hasslacher Co., New York City
Treasurer: Donald McKesson, McKesson & Robbins, New York City
Board of Governors:
  Vice Presidents, *ex officio*
  August Merz, Heller & Merz, Newark, N. J.
  F. P. Summers, Noil Chemical & Color Works, New York City
  S. Iserman, Chemical Co. of America, New York City
  F. E. Signer, Butterworth-Judson Corp., New York City
  W. T. Cashman, Grasselli Chemical Co., Cleveland, Ohio
  S. W. Wilder, Merrimac Chemical Co., Boston, Mass.
  A. S. Burdick, Abbott Laboratories, Chicago, Ill.
  Donald McKesson, McKesson & Robbins, New York City
  F. L. McCartney, Monsanto Chemical Works, St. Louis, Mo.
  James T. Pardee, Dow Chemical Co., Midland, Mich.
  Chas. H. Herty, *ex officio*

The Carbon Electrode

The National Carbon Company has issued a little booklet of 79 pages dealing with the carbon electrode. In addition to an account of the history and a description of the manufacture of carbon electrodes, the booklet contains electric furnace diagrams, standard electrode data, physical and mechanical properties of carbon, and various formulas and tables which should prove of value to the users of electric furnaces.

A. C. S. Division and Section Meetings

DIVISION OF AGRICULTURAL AND FOOD CHEMISRTY

The Division of Agricultural and Food Chemistry held two long sessions on Wednesday with T. J. Bryan, *Chairman*, presiding. Of the 21 papers on the program all were read and discussed except three which were read by title in the absence of the authors. The papers on self-rising and bleached flours promoted very active and interesting discussion. The authors of these papers showed that flours low in gluten were being used very extensively in the South and that in some instances leavening agents were not present in proper proportions to obtain the best results. The paper by B. B. Ross on "The Occurrence and Composition of Some Alabama Phosphates" was very interesting and showed plainly that there were large and rich deposits of this phosphatic material in Alabama awaiting development. A paper by Dr. E. H. S. Bailey of Kansas on a dietary study of some state institutions showed the necessity for such investigations and that more such investigations should be made of the various institutions of several states. Mr. F. W. Robison brought out the fact that a new electric method of treating milk produces a product which is better than the pasteurized milk that is ordinarily produced.

The meeting as a whole was unusually well attended and more interest in discussion was shown than has been seen for some time. At Pittsburgh next fall the Division will devote one full session to a symposium on food fats, with Dr. David Wesson as Chairman.

C. S. Brinton, *Secretary*

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DIVISION OF BIOLOGICAL CHEMISTRY

In the absence of the Chairman, Howard B. Lewis, who was unable to attend the meeting on account of sickness, Secretary J. S. Hughes presided at the meetings of the Division. During the morning session eight very interesting papers covering a wide range of subjects were presented. Of these the one presented by Atherton Seidell, in which he discussed some of his difficulties in attempting to isolate Vitamin B, was very interesting and called forth some discussion very helpful to people working in this field. At the afternoon meeting five papers were presented. Three of these were on the subject of vitamins, two by J. S. Hughes concerning the effect of feeds low in vitamins on domestic animals, the other by C. H. Hunt on Vitamin C contained in goat's milk. These papers were received with the interest always accorded the papers on this very interesting subject. One of the most interesting and timely papers of the entire meeting was that by I. K. Phelps on "The Decomposition of Food by *Bacillus botulinus*." In discussion of this subject Dr. Phelps gave a very full and interesting report of a number of cases of botulinus poisoning which had occurred recently. At the meeting in New York last fall a committee, of which Dr. A. D. Emmett was Chairman, was appointed for the purpose of devising some standard method of feeding and caring for experimental animals to be used in the study of the nutritive properties of foods. Dr. Emmett was unable to attend the meeting but submitted a report for the committee. This report states that progress has been made but as yet no definite methods can be suggested for this work. Reports at future meetings will be received on this subject.

J. S. Hughes, *Secretary*

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DIVISION OF DYE CHEMISTRY

Before starting the papers the Secretary of the Division enumerated a few of the activities in which the officers of the Division had been engaged since the last meeting. In accordance with the resolution of the Division at the Rochester Meeting in the spring of 1921, the Secretary of Commerce was petitioned to supply the information on individual dye marks that had been elided from the Norton Census of Dyes because of the protest of the importers of German dyes. In accordance with this resolution the Bureau of Foreign and Domestic Commerce prepared a supplement to the Norton Census, giving this desired information. These supplements have been distributed to all registered members of the Division and also to other interested parties.

The Secretary of the Division has also been coöperating with the Society of Dyers and Colourists of Bradford, England, in the preparation of the Color Index. The Coöperation Committee of the Division had one meeting in the early winter with the Color Laboratory in Washington and the report of this visit was made to the Division.

Several men were prevented from attending and their papers were read by title. Dr. Max Phillips of the Color Laboratory in Washington read a paper by himself on "The Preparation of 7, 7′-Di(-hydroxy-isopropyl)-indigo," and he also presented a paper by Mr. H. L. Haller of the same laboratory on "The Preparation of Phenylglycine-*o*-carboxylic Acid. I—From Anthranilic Acid and Monochloroacetic Acid." Dr. E. Emmet Reid of Johns Hopkins spoke about some work which he and Mr. Waldron had been doing on azo dyes containing sulfur. Dr. Reid exhibited samples of dyeings showing that when sulfur was in a position directly bound to the benzene ring its influence was to deepen and redden the shade of azo dyes. Dr. M. T. Bogert described work which he and Dr. Meyer had done on "Experiments with Dehydrothio-*p*-toluidine and Related Compounds." Dr. Bogert announced that quite recently he had prevailed upon Columbia University to relieve him of all his work except that pertaining to dyes, intermediates, and related compounds. Dr. Jules Bébie described a number of uses for the saccharin by-product, *p*-toluenesulfonyl chloride. "The Analysis of β-Naphthylamine" by a number of different methods was described by Messrs. Henry R. Lee and D. O. Jones.

R. Norris Shreve, *Secretary*

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DIVISION OF INDUSTRIAL AND ENGINEERING CHEMISTRY

The practice of the Division of Industrial and Engineering Chemistry of holding a symposium upon a subject of vital importance to industrial chemists is proving extremely valuable. At Birmingham the subject was "Distillation," and the interest in it was demonstrated by the fact that over one-third of the chemists present at the Convention were in attendance at the meeting. Papers giving the fundamentals underlying the subject were presented. The applied phases of the topic were also well covered. W. A. Peters, Jr., was chairman of the symposium, and he is to be highly commended for arranging such a well-balanced set of papers. Many papers were promised to him by chemists, who later found that their firms did not wish them to present papers at this time. The papers presented before the symposium will be published in the June issue of This Journal.

Many papers on the general program dealt with gases and fuels; those by Drs. Fieldner and Parr provoked considerable discussion. The tendency to draw specifications for everything was discouraged in a paper by Dr. Collins. Reliable brands often mean more than detailed specifications. Mr. Shreve's paper showed by statistics how an American potash industry, if given a brief period of protection, would become a very valuable national asset. At last a scientific attack on the subject of whitewashes has been begun, and some valuable results and conclusions were given by Mr. Fink.

At the business meeting of the Division it was unanimously voted to recommend to the Society that a Section on Gas and Fuel Chemistry be created at the Pittsburgh Meeting. Reports were read from the following committees: Lime Committee (progress reported); Standardization of Apparatus and Material Committee (progress reported); Methods of Analysis and Specifications of Commercial Soaps and Soap Products (committee presented final report which was referred to the Advisory Committee). The Acting Secretary was unanimously elected Secretary of the Division. Automatic Process Control is the subject upon which the symposium will be held at Pittsburgh.

E. M. Billings, *Secretary*

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DIVISION OF ORGANIC CHEMISTRY

Of the 34 papers on the program, 29 were presented. Although the attendance was small, averaging about 30, the discussion of the papers was unusually lively. This may have been due to the fact that abstracts of all the papers had been mailed to the members about ten days before the meeting. Among the papers which aroused the most discussion, were the following: Dr. Gilman's paper on the "Preparation of the Grignard Reagent;" "Catalytic Reduction of the C-N Complex," by De Witt Neighbors, S. M. Clark, J. E. Miller, A. L. Foster and J. R. Bailey; and Dr. Hibbert's paper on "Crotonaldehyde." The regular papers of the Division were followed by a symposium with the Cellulose Division on the recent work on the constitution of starch and cellulose. Dr. Hibbert gave a very lucid discussion on recent work in this field, especially that of Helfrich. Dr. Mahood continued the discussion, giving the recent work of Haworth and Irvine on the disaccharides. He also gave at some length the work of Kurt Hess on the structure of cellulose. Dr. Hibbert called attention to the flaws in the work of Hess, as shown by the results of Freudenberg, Karrer, and others. He also gave a discussion of his own cyclic formula for the nucleus of cellulose, pointing out its strong points and its weaknesses. The small number of chemists registered in the Organic Division does not adequately represent the organic chemists of the country. The Secretary will be very glad to receive suggestions for methods of reaching organic chemists and for the names and addresses of any chemists likely to be interested in the work of the Division. Such suggestions and names should be sent to the Secretary, Northwestern University, Evanston, Ill.

Frank C. Whitmore, *Secretary*

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DIVISION OF PHYSICAL AND INORGANIC CHEMISTRY

The Division held three very interesting sessions, at which 26 papers were presented. They joined with the Division of Industrial and Engineering Chemistry for their symposium on distillation Wednesday morning. At the business meeting of the Division, after considerable discussion of possible methods of arranging the program, it was voted that the arrangement be left to the discretion of the Secretary, with instructions to place related papers together on the program, regardless of their priority of receipt or, within reason, of the number of papers offered by one individual.

Professor Bingham gave the following report, as Chairman of an informal committee nominated this year to consider the perpetuation of the *Journal of Physical Chemistry:*

> Whereas, arrangements have been made whereby the *Journal of Physical Chemistry* will be continued and probably internationalized, and
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> Whereas, the continuation of the *Journal of Physical Chemistry* is of importance to all chemists, especially those interested in special fields of physical chemistry, such as colloid chemistry, adsorption, surface catalysis, capillary chemistry, etc., as a medium of more extended publication of research than can be printed with the present funds of the Society in the *Journal of the American Chemical Society*, and
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> Whereas, it has been suggested that the *Journal of Physical Chemistry* be published under the auspices and direction of the American Chemical Society and The Chemical Society (London), and
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> Whereas, it is desirable that all scientific chemical activity in America, so far as possible, shall be centered within the American Chemical Society,
>
> *Therefore be it Resolved*, that the Division of Physical and Inorganic Chemistry recommend to the Council that the officers of the Society be instructed to correspond with The Chemical Society, and to arrange, if possible, for the appointment of an editor and a board of editors and, if necessary, a board of control, by the American Chemical Society alone, or in conjunction with The Chemical Society, to take over and direct the future of the *Journal of Physical Chemistry*, if it can be done without expense to The Chemical Society.
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> *Be it Further Resolved*, that an arrangement be made with the Board of Control of the *Journal of Physical Chemistry* whereby members of the American Chemical Society and of The Chemical Society, if the latter society jointly acts with the American Chemical Society in the matter, may receive a reduced rate of subscription over that extended to nonmembers of these societies.

After considerable discussion it was voted that (subject to the written approval of the report by the majority of the members of the special committee) the Division should recommend to the Council that the Society adopt the plan outlined in the committee report.

Among the papers which attracted special interest were those of Sosman and of Wherry bearing on the structure of solid crystals; of Franklin on ammono-nitric acid. Edgar and Schuyler gave interesting data on the equilibrium in the vapor phase between acetic acid, alcohol, and ethyl acetate which cleared up certain apparent contradictions in previously reported studies on the catalysis of this reaction in the vapor phase.

W. A. Noyes and J. T. Wilson reported accurate data on the ionization and general behavior of hypochlorous acid, bearing upon the possible existence of a positive chlorine ion.

R. E. Wilson, *Secretary*

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DIVISION OF RUBBER CHEMISTRY

R. P. Dinsmore presented a paper on "Internal Mixers" which summed up his experience. He left the audience much undecided as to the advisability of the general application of this type of mixer. Ira Williams, in his paper on "The Thermal Properties of Rubber and Rubber Pigments," showed very careful work on diffusivities and conductivities of rubber, fabric, and pigments.

H. W. Greider showed that magnesium carbonate ranks near zinc oxide and carbon black as a filler, nine volumes to one hundred volumes of rubber being the optimum amount and also the maximum advisable in most cases. High set restricts its use. The paper of Norman A. Shepard and Stanley Krall covered experiments with common organic accelerators. With a compound consisting of 48 parts of rubber, 48 of zinc oxide, and 3 of sulfur they secured equivalent cures at 60 min. at 141° C. as determined by coinciding stress-strain curves with the following parts of accelerator: 0.5 of hexamethylenetetramine; 0.25 of *p*-nitrosodimethylaniline; 0.75 of aldehyde ammonia; and 1.5 of thiocarbanilide. True coefficients of vulcanization were determined. Wide variations were found. The authors reached the conclusion that there is no relation between the coefficient of vulcanization and physical properties.

W. B. Wiegand presented standard forms and methods of plotting data. W. W. Evans announced that the rubber division methods of analysis are ready for publication and will come up for adoption at the September meeting. The Geer age test was adopted as standard.

The incorporation of chemical tests in specifications for hose, insulated wire, etc., was opposed by several members. It was the feeling of those present that specifications should be limited to physical and life tests. The present specifications are restricting development. About 35 were in attendance.

C. C. North, *Acting Secretary*

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DIVISION OF SUGAR CHEMISTRY

The Division of Sugar Chemistry held its sessions on Wednesday and Thursday, S. J. Osborn, *Chairman*, presiding. The attendance showed a good representation of all important branches of the industry and even included one visitor from the Island of Mauritius, who presented a paper. Great interest was shown in the work of the Division and progress was reported on many of the problems which had been recently receiving attention at the hands of the sugar chemists and technologists. "The Manufacture of Plantation Standard Granulated Sugar with and without Activated Char" was ably summarized by Professor Coates, and other papers on the properties of boneblack and decolorizing carbons showed that the interest in this subject still continues and that there is much further work yet to be done. The measurement of color was covered by papers read by H. H. Peters, reporting investigations of himself and others at the Bureau of Standards on the fundamentals of the problem, and Dr. F. W. Zerban gave some data regarding the color range of cane sirups. Dr. C. A. Browne presented some interesting figures on the "Moisture Absorptive Power of Different Sugars and Carbohydrates," showing that some commonly held ideas needed revision. Dr. J. F. Brewster had some interesting data on "The Control of Reaction in Sugarhouse (and Refinery) Liquors" and the composition of the precipitate formed in sugarhouse sirups. Mr. W. P. Valentine described and exhibited an improved precision refractometer for the sugar industry which was favorably commented upon by those interested in refractometric determinations. The rare sugars were represented in a paper by Mr. R. S. Black on "The Preparation of Adonitol." Analytical methods were discussed in several papers, of particular interest being the case reported by M. H. Wiley on "The Observance of Mutarotation in the Polarization of Raw Cane Sugar."

S. J. Osborn, *Chairman*

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DIVISION OF WATER, SEWAGE, AND SANITATION

While the attendance at the meeting of the Division of Water, Sewage, and Sanitation was smaller than at any meeting during recent years, there being only 26 in attendance, the interest and enthusiasm were greater than usual. The program was most interesting and the papers were fully discussed. This was especially true of the paper by Bartow, Flentje and Gallaher on "The Effect of Temperature on the Rate of Reaction in Water Softening by the Lime-Soda-Ash Method," a topic of peculiar interest to the chemist at present interested in water supplies and water treatment plants.

The paper by Hatfield on the "Application of pH Value to the Operation of Filtration Plants" was also well received and thoroughly discussed.

The Chairman, Dr. A. M. Buswell, made a full report on the activities of the committee from the American Chemical Society appointed to coöperate with a similar committee from the American Public Health Association to revise the standard methods of analysis issued by the latter association.

Owing to the extended discussion of the formal papers time was not available for consideration of the special topic for discussion, namely, Specifications for Lime for Water Treatment. Accordingly, the Division voted to defer this topic until the fall meeting.

In the afternoon the Division was entertained by an automobile trip to the Birmingham Pumping and Filtration Plant, located about ten miles northeast of the city. Visitors to the plant freely expressed the opinion that it was one of the best arranged and best equipped plants that they had ever inspected.

W. W. Skinner, *Secretary*

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SECTION OF CELLULOSE CHEMISTRY

The attendance at the meetings of the Section was very good, and the full discussion of the papers presented indicated unusual interest in the subject of cellulose chemistry. After some revision, the report of the Standard Cellulose Committee outlining a method for the preparation of a standard cotton cellulose for research purposes was adopted. The Committee on Analytical Methods reported progress and announced that its final report would be ready for the next meeting. The Viscosity Measurement Committee reported that further study of the falling ball method in comparison with other methods was being made and that a report would be submitted at Pittsburgh. The report of the Treasurer, showing a substantial cash balance on hand, was adopted. The papers covering the report of work done at the Forest Products Laboratory showed that nine additional species of American woods had been analyzed. The results of this series of investigations as a whole show that the woods fall into two classes on a basis of their constituent groups, which correspond to the botanical divisions, broadleafed trees and conifers.

A study of the products obtained by the hydrolysis of spruce cellulose with dilute sulfuric acid established the very important fact that this cellulose does not yield glucose exclusively on hydrolysis, but a mixture of glucose and mannose.

The investigation of sugar formation in a sulfite digester shows that sugar production is most rapid between the seventh and ninth hours of the cook, during which time the chips are disintegrated. The sugar formation increases with increase of the free sulfur dioxide content of the cooking liquor. The maximum formation of sugar with minimum loss of pulp occurs at about the twelfth hour. Studies on the formation of galactose obtained by the acid hydrolysis of western larch wood have demonstrated that this sugar, which, under the conditions hitherto employed, had not been fermented, can be converted into alcohol by adding an autolyzed yeast nutrient to the fermentation liquor and maintaining a low acidity during fermentation. This procedure increases the yield of ethyl alcohol from western larch by approximately 100 per cent.

Further comparative tests on the procedures of Schorger and of Sieber and Walter for the determination of cellulose by chlorination show that the lower yields obtained by the latter are due to too concentrated a stream of chlorine and that comparable values may be obtained by diluting the chlorine with an equal volume of air in the latter procedure.

Progress has been made, as indicated by the papers on the subject, in the synthesis of acetal derivatives and of simple bodies of the polysaccharide type which promise to throw much light on the chemistry of cellulose.

The symposium on the production of cheap cattle foods by acid or alkaline treatment of waste cellulosic materials showed considerable advance in this field. Sawdust, hydrolyzed with 1.8 per cent sulfuric acid, yields a product which feeding experiments show is a good substitute for barley or corn in a grain ration. Straw with an edible content of 8 to 10 per cent can be made to yield a feed with an edible content of 56 per cent by the simple treatment of heating it in chopped form with 8 per cent of its weight of a 1 per cent soda ash solution.

S. A. Mahood, *Secretary pro tem*

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SECTION OF CHEMICAL EDUCATION

The Section on Chemical Education opened sharply at 9:30 on Wednesday morning with Dr. Edgar F. Smith as Chairman. After a few remarks by Dr. Bingham on the important role which a teacher may play in the extension of the metric system, the morning was given over to "An Ideal First Year Course in Chemistry." A paper by Wilhelm Segerblom on high school chemistry and a discussion of college chemistry by William McPherson started a very interesting meeting. Many participated in the discussion, with the result that the Section purposed to do something if possible to bring about a better correlation of high school and college chemistry.

The Wednesday afternoon meeting was opened by an interesting talk by W. K. Lewis on "Studying Chemical Engineering by the Unit-Operation Method." The advantages and disadvantages were clearly shown, with the result that the former far outweighed the latter. The paper by Dr. Daniel and the interesting remarks by Drs. Desha and Williamson, Jr., raised some very healthy discussion in regard to chemical engineering education. Two outstanding conclusions were: (1) the courses offered by different universities in chemical engineering are far from uniform, and (2) the chemical engineer needs a broader education before he begins to specialize.

On Thursday morning the meeting was opened by Dr. Bogert. He described some of the new organic courses which are now available at Columbia University. Dr. Swan spoke next on "A Book and a Battery." His remarks were extremely interesting from a historical standpoint. Dr. Cuno showed how the teaching of organic chemistry might be simplified and forcefully taught by means of charts. Dr. Webb gave some of his findings on standard tests with the purpose of sounding out the chemists as to their desires in the extension of standardization work in chemistry. From encouragement received at the meeting, he will continue his work and report again at some future meeting of the Section. Dr. Montgomery gave his experience in teaching unified courses in chemistry. Dr. Mahin's paper on "Science or Athletics?" brought forth a flood of discussion, and as a result a motion was passed to ask for the paper's release from the Society, in order that it might be published in some paper where it would reach the hands of the most teachers.

Neil E. Gordon, *Secretary*

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SECTION OF HISTORY OF CHEMISTRY

The meeting of the Section on the History of Chemistry was attended by over one hundred chemists. A large amount of interest was manifested in the program, which was devoted principally to a discussion of the early chemists and chemical industries of America, more particularly of those in the South. President Edgar F. Smith opened the program with an entertaining address upon the life and work of Dr. Thomas Cooper who for many years was professor of chemistry at the South Carolina College at Columbia.

Rev. George L. Coyle read a paper upon the work of Father Athanasius Kircher, a seventeenth century scientist distinguished for his opposition to alchemy and the many-sidedness of his attainments. The paper of Ralph H. McKee upon "Some Photographic Reminiscences of the Priestley Centennial of 1874" was presented with photographs by the Chairman. A letter from S. P. Sharples was read describing the Centennial Meeting which resulted afterwards in the formation of the American Chemical Society. John N. Swan exhibited one of the early electric batteries used by Sir Humphrey Davy and spoke of Davy's work upon the electrolysis of the metals of the alkalies and alkaline earths. J. A. Gunton showed an early chemical slide rule and gave an account of its origin and use. William McPherson spoke entertainingly upon reminiscences of celebrated Italian chemists. C. A. Browne read a paper on sources of information upon early chemistry and chemical industries in America. He mentioned as among the earliest pieces of chemical work performed in America the assay of silver ores by Spanish explorers in Arizona in 1598. B. B. Ross spoke upon the early indigo, sugar, naval stores, and other chemical industries of the South. The first plant for artificial refrigeration in the United States was established by Dr. John Gorrie of Apalachicola, Florida (patented 1850). Dr. Ross spoke also of the early work of Prof. John Darby at the East Alabama College, now the Alabama Polytechnic Institute, and exhibited a Berzelius alcohol lamp used by him. A paper by Elton R. Darling described the early salt industry of the Ohio River and Kanawha Valley. In the absence of Dr. Eugene A. Smith his paper upon early southern chemists was presented by Prof. S. J. Lloyd of the University of Alabama. The various papers and addresses were supplemented by exhibits of rare books, letters, photographs, and apparatus. President Smith in summing up the work of the Section made a strong plea for historical chemical research in America in the different sections of the United States.

C. A. Browne, *Chairman*

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SECTION OF PETROLEUM CHEMISTRY

The sessions of the Section were well attended in proportion to the size of the meeting and were marked by interested and pointed discussion of the papers presented, as well as of the question of policy and business, which came up for attention. Theoretical aspects of petroleum science were considered in papers on the viscosity of fluids, presented, respectively, by W. H. Herschel and W. H. Fulweiler, and in one paper on surface tension of oils by C. K. Francis. The practical sides of oil technology were considered in R. R. Matthews' paper on the corrosion of refining equipment, in the discussion of volume changes in petroleum products by A. P. Bjerregaard, and in a paper on natural gasoline recovery by F. M. Seibert and F. E. Hosmer. Petroleum education was discussed by Edwin DeBarr and F. W. Padgett.

The discussion of policy of the Section in formulating divisional by-laws brought out a resolution that, while every phase of petroleum chemistry should be open to the Section, it would be advisable to avoid the writing of specifications and the formulation of standard methods of testing. In the Conference on the Promotion of Research on Petroleum, in which the American Petroleum Institute was represented by Dr. Van H. Manning, an endorsement was made of the research objects of the Petroleum Institute, as described by Dr. Manning, and it was decided to appoint a committee, which should include representatives of the National Bureaus of Standards and Mines, to coöperate vigorously with Dr. Manning in promoting a joint research program on the "Chemistry and Chemical Technology of Petroleum."

W. A. Gruse, *Secretary*

A. C. S. Committee Reports

REPORT OF COMMITTEE ON EMPLOYMENT BUREAU

Your Committee appointed to consider the taking over of the Employment Bureau of the Chemists' Club by the American Chemical Society or to establish a bureau of its own to replace this organization, begs leave to submit the following report.

Your Committee appreciates the importance of the whole subject of employment. There can be no question as to the desirability of the establishment of some adequate provision whereby the chemist and the individual desiring the services of the chemist may be brought together to their mutual advantage. The vital question, therefore, is what is the best arrangement for securing the desired ends. A number of plans have been proposed.

Plan A—The present Employment Bureau of the Chemists' Club may be taken over by the American Chemical Society and expanded so that it will serve the Society as a whole. Such a bureau, if established, would have to be either (1) a free employment agency, or (2) a paid employment agency.

The vital question in connection with the free employment agency plan is the financial one. What will the plan cost the Society? Some idea can be obtained from the experiences of the Bureau of the Chemists' Club. This Bureau was incorporated in 1913 and has registered since that time 7356 different individuals and has filled 1955 positions. Its expenditures in its early years were about $7000, increasing with the larger patronage to approximately $10,500 for the year ending May 1921. It is probable that if the Bureau were increased to serve the whole Society these expenditures would at least be doubled. The Federated American Engineering Societies have a budget of $17,900 for the present year for their Employment Agency. The American Association of Engineers, with a highly organized agency and a number of branches, spends about $30,000 for a similar purpose. The adoption of this plan would therefore necessitate an expenditure on the part of the Society of at least from $15,000 to $20,000 per annum.

The Society, on the other hand, may adopt the paid agency plan. If this is done, however, it will be practically necessary to form a separate corporation. Otherwise, the Society will become subject to a number of taxes, including both national and state income taxes.

Plan B—The Society may establish a separate corporation and run a paid agency. Judging from the experience of the Chemists' Club and teachers' agencies, it would seem a probable assumption that such an agency could be made self-supporting unless in times of great depression like the present. The Bureau of the Chemists' Club has been self-supporting until the present business depression.

Plan C—The various Local Sections may finance and operate employment bureaus for their own members as is done in a few cases at present.

In this plan the Society would have no financial interest whatever. Each Local Section would finance its own agency in whatever way it desired. One advantage of this plan would be that each agency would serve a more or less restricted community and hence could know its patrons better and be in a better position to recommend the right man for the right place. On the other hand, it has a disadvantage in that there are a number of members of the Society who belong to no Local Section and hence would be left out in such a plan.

Plan D—The various Local Sections may operate their own bureaus as proposed in Plan C, but in addition there may be operated a central office, limited in its scope but able to serve the members of the Society who do not belong to any Local Section, and in a general way to coöperate with the bureaus of the Local Sections. Such a central office could be located preferably at Washington, under the supervision of the Secretary of the Society or the Editor of the *Journal of Industrial and Engineering Chemistry*. The expense of such a plan would be a nominal one, certainly not to exceed $4000 or $5000.

Plan E—The Society may unite with the Federated American Engineering Societies in the establishment of a general employment bureau.

Believing it to be outside its jurisdiction, the Committee has made no effort to ascertain whether or not the Society would be welcomed as a member of the Employment Bureau of the Federated Societies.

Plan F—The Society might interest appropriate individuals in the plan of starting a paid employment bureau for chemists to be operated for profit on the same general plan as a teachers' agency. In operation of this plan the Society would have no part except a sympathetic interest.

This plan would probably be acceptable to the members of the Society (and the number seems to be large) who believe that the Society ought to have nothing whatever to do with the employment bureaus, that the average individual who secures employment through an agency is apt to be disappointed, and that on the whole the Society would make more enemies than friends by maintaining an employment bureau.

The question submitted to the Committee is one that is of such vital interest and also one concerning which there are such strong and divergent opinions that the Committee has thought it unwise at this time to make any final definite recommendations but submits the following for general consideration:

1—That the Council be asked to consider the various plans proposed or any additional plans not listed above with a view to finding out which one of these plans, if any, is desirable.

2—That, after a full consideration by the Council, this report, together with such instructions as the Council may care to give, be referred back to the Committee or to a new committee for further consideration and report at the next meeting of the Society.

Wm. McPherson, *Chairman*

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REPORT OF COMMITTEE ON OCCUPATIONAL DISEASES IN THE CHEMICAL TRADES

This year the Committee has been unfortunate in the loss of its Chairman, and in consequence thereof has found itself, when confronted with the problem of preparing the report, in a chaotic frame of mind.

The past year has brought us face to face again with certain occurrences and facts in the field of occupational diseases and industries, and especially with reference to their causation and prevention.

The letter files of the Committee have grown considerably, and this can be taken as an indication that the chemical and allied industries consider more seriously occupational hazards and diseases as truly economic items.

The enlightened viewpoint is the result of many factors working in the same direction, some for the protection of the employees and others for the protection of employers.

In this spirit of better progress a greater tendency prevails, on the part of the industries, to employ more physicians and hygienists, and many concerns who heretofore regarded sanitarians as a luxury not to be indulged in now find it a valuable arrangement.

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The time has come when we are realizing that something more is necessary in this work than the sole qualification of being a doctor of medicine. We are now in the age of prevention and not in one of an expectant industrial pathology. Consequently we must expect our physicians and others trained in industrial hygiene to be basically trained for this kind of work. We are also conscious of the fact that each industry presents its individual hygienic problems which can be worked out only when the physician is actually a member of the force in the particular chemical factory.

* * * * *

Our hygienists must further be able to think of how the particular chemical will affect the human body, of the means at hand for rendering first aid, and, in the case of the physician, of after-treatment for casualty cases.

A spirit of coöperation must always obtain between the superintending chemist and engineer and the industrial hygienist and physician in order to get the best results. Each possesses special knowledge which, when properly associated, will tend to keep industrial hazards down to a minimum.

To-day, various universities and colleges offer courses in public health and industrial hygiene. * * * * * Some of the courses are intended for persons who do not aspire to the degree of doctor of medicine, and lead to the bachelor's degree or a higher collegiate degree, or to the doctorate in public health or a similar qualification. Other courses are open only to medical undergraduates and are counted toward the partial fulfilment of the requirements of the doctorate in medicine, or may be taken by graduates in medicine, with other work, as a course leading to a certificate or to a degree in public health. The chemical manufacturer can select a person skilled in preventive medicine or one who has the added qualification of treating injuries and diseases as they arise.

Many concerns do not employ a full-time hygienist or physician, believing it an economic waste. An arrangement of this kind, while often remunerative for the physician, is very unsatisfactory from the standpoint of industrial hygiene. * * * * * The part-time physician has no time for constructive thinking, particularly when he is chiefly engaged in an extensive outside practice.

Another step in the right direction would be to include a set of lectures on industrial hygiene in every course in chemical engineering. This, we believe, would go far toward removing some of the more flagrant, and sometimes easily removable, conditions in existence. By this we do not mean that the chemist or chemical engineer should function as a hygienist, but the knowledge gained would certainly increase his scope of view and avoid many errors and misunderstandings which now occur.

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Making careful functional examinations of the hearts of employees is emphasized by C. Phipps [*J. Am. Med. Assoc.*, **78** (1922), 562] on the basis of his findings of 650 persons for the Massachusetts Industrial Accident Board in the Workmen's Compensation Act. Out of this number 231 showed abnormal heart conditions.

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Defective vision among industrial workers, from the viewpoint of economic loss to the respective industries, is discussed by McCord and Lyle [*J. Am. Med. Assoc.*, **78** (1922), 606] on the basis of observations made in a plant engaged in the manufacture of cotton braids.

We often meet with men in chemical plants who foster the belief that wearing glasses for correcting errors of vision constitutes an admission of incapacity to conduct the tasks assigned. "The industrial physician in his dual function of serving employee and employer advances the interests of each through the careful supervision of the eyesight of all workers."

Gassing of the eyes, frequently observed among still cleaners in oil refineries, causes a blinding, painful inflammation of the conjunctiva and is said to be due to sulfur compounds in the oils. The practice of workmen in applying raw potato juice or any other poultice to the eyes in such cases is deplored by the *Journal of the American Medical Association* [**76** (1921), 1031]. G. M. S., in the same *Journal*, finds the instillation of a 1 per cent solution of holocaine and the greasing of the lids of value. * * * * *

Carbon monoxide, according to Wilmer [*Am. J. Opthalmology*, **4**, 73], causes ocular paralysis, heminaopsia (blindness of one-half of the visual field, affecting one or both eyes), and inflammation and degeneration of the optic nerve. The treatment resolves itself into remedies suggested by the various symptoms, and especially prophylaxis and hygiene.

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Detailed directions are given for the treatment of acid and alkali burns by Smith [*Modern Medicine*, **3** (1921), 232]. The strong caustics, as "sulfuric acid, nitric acid, potash, chloride of antimony, chloride of zinc, acid nitrate of mercury, bromine, chromic acid, lime and (hot iron)," are discussed.

A report on an outbreak of zinc chloride poisoning among the workers in a wood preserving industry, made by McCord and Kilker [*J. Am. Med. Assoc.*, **76** (1921), 422], again emphasizes the need of a little foresight in preventing local lesions due to handling chemicals, etc. * * * * *

Three other types of lesions were observed: a tar dermatitis (2 cases), attributable in part to preparations used in cleaning up, benzene, light and heavy oils from coal-tar distillation; tar acne, present in varying degrees in all the employees examined, and probably due to a collection of tarry matter in the hair follicles and occurring especially on the forearms; tar cancer, or a condition suggesting it, which was found in two cases. The quick disappearance of the lesions suggests caution in the pronouncement of cases as tar cancer. Deelmann [*Nederlandsch Tijdschrift Geneeskunde*, **2**, No. 20, 2395; abst. *J. Am. Med. Assoc.*, **78** (1922), 696] believes tar coming from horizontal retorts more active than tar from vertical retorts, since malignant degeneration occurs sooner. Bloch and Dreifuss [*Schweiz. mediz. Wochenschr.*, **51**, No. 45, 1033] conclude the cancer-producing substance to be in a fraction which boils at over 300° C.

Under the caption "So-called Aniline Tumors of the Bladder," Alice Hamilton [*J. Ind. Hyg.*, **3** (1922), 16] calls attention to hydrogen arsenide as a possible etiologic factor, since hydrogen arsenide poisoning is admittedly present in all conditions with which the bladder tumors of aniline workers have been associated. * * * * *

An epidemic lung disease, "Schneeburg lung cancer," which is found among many workers in the cobalt mines of Saxony, is again up for discussion. Uhlig [*Arch. path. Anat. Virchow's*, **230** (1921), 76] mentions how common it is to find men in the prime of life so affected and relegated to very light work. Arsenic is believed to be responsible for the condition. * * * * *

A dermatosis, called "ink poisoning" by printers, which affects those parts of the arms and hands subject to constant contact with colored inks, is known to have prevailed for many years among printers in the large printing and engraving plants. The workers believed green ink to be more irritant than the other colors. McConnel of the U. S. Public Health Service [*Pub. Health Reports*, **36**, 979] stresses the fact that all inks, irrespective of color, when removed by the brutal methods in vogue in the establishment at the time, are liable to cause an irritation which may lead to a dermatosis. * * * * *

An acute dermatitis of the face, hands, and forearms was noted among the women workers on phenol resins by Sachs [*Weiner klin. Wochschr.*, **34** (1921), 356], and many of the patients also presented symptoms of conjunctivitis and some bronchitis. Vapors of ammonia, phenol, and formaldehyde were noted in the room. The treatment given is described.

The part played by the skin in lead poisoning was investigated by Sussmann [*Arch. Hyg.*, **90**, 175], who found the main channels for absorption of lead to be the lungs and alimentary canal rather than the skin. Shie [*J. Am. Med. Assoc.*, **76** (1921), 835] makes the statement, "By far the greatest amount of lead poisoning occurs among the industrial workers," and gives the result of his investigations on more than 900 workers exposed to the lead hazard. * * * A refinement of the system of prophylaxis is necessary before the morbidity rate can be lowered.

Alice Hamilton [*J. Am. Med. Assoc.*, **78** (1922), 627] calls attention to the growing menace of benzene poisoning in American industries. Since benzene is a more powerful solvent than petroleum benzine or naphtha, for fats, gums, and resins, and is now below the latter in price, there is double temptation to use it. Perhaps the petroleum distillates will be supplanted by the coal-tar in the making of varnish, quick-drying paints, and shellacs, and in dry cleaning, if not in the making of spread rubber goods, as is done in Europe. Unless precautions are taken, severe and fatal cases of poisoning are bound to occur during the distillation of benzene and the cleaning of apparatus employed in the process. * * * * * Preventive measures are suggested, but in many cases it is a very difficult matter to instal certain necessary systems of prevention.

According to Minto and Smith [*Arch. Internal Med.*, **28**, 687], tetrachloromethane poisoning may be predicted from an examination of the blood.

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Only a passing reference can be made to the very important work on carbon monoxide poisoning reported during the past year. The literature has assumed large proportions, as can be judged from the article by Henderson [*J. Ind. Eng. Chem.*, **14** (1922), 229]; *Bulletin* **291** recently issued by the U. S. Bureau of Labor, with A. Hamilton as the author, and the survey of carbon monoxide poisoning in American steel works, metal mines and coal mines by H. S. Forbes [*J. Ind. Hyg.*, **3** (1922), 2].

* * * * *

Progress has been made in the adoption of the term "methanol" for methyl or wood alcohol. Ziegler [*J. Am. Med. Assoc.*, **77** (1921), 1160; *Penn. Med. J.*, **25**, 177], among others, advocates the use of the term, and furthermore states that three factors should induce manufacturers to abolish the use of wood alcohol and substitute denatured alcohol: humanitarianism, self-interest, and practical economy.

Satisfactory casualty and morbidity statistics of the chemical and allied industries are not now available. It is obvious that a true picture of our economic losses from this source will never be obtained until a better spirit of coöperation exists between the manufacturer, the Committee, and public and private officials charged with this work.

It is a pleasure to know that the National Safety Council is taking a census of safety men in the chemical industry, as well as in other industries and in public safety work.

Owing to the usual lack of finances, the Committee was unable to coöperate properly with similar committees of other private technical and scientific organizations and in a previous report attention was directed to the imperative need to-day of an "Institute on Occupational Diseases and Hazards" to serve as a clearinghouse for information and direction in this field of endeavor. Such an institution would be of inestimable value for all connected with the chemical and associated industries. Much information could be collected from private, governmental, and educational sources, and through the institute made readily available to all.

It is recommended that the incoming committee direct some of its efforts to settling upon a tangible basis for obtaining funds for creating the institute.

The Committee also feels that much time could be saved by collecting all excerpts of articles on vocational hygiene, etc., in a special column of *Chemical Abstracts*, and by inserting cross references in other appropriate columns. We feel sure that with such an arrangement information on the subject would receive better attention.

LEWIS WILLIAM FETZER,
Chairman pro tem

REPORT OF COMMITTEE ON INDUSTRIAL ALCOHOL

Your Committee on Industrial Alcohol was appointed by President Smith soon after the Rochester Meeting last April as the result of a resolution adopted at that meeting.

On April 25, 1921, Mr. Volstead introduced a bill, H. R. 5033, in the House of Representatives which if passed would have seriously crippled the industries of the country depending upon legitimate uses of alcohol.

A telegraphic summons brought the Committee together in New York, where general resolutions in the name of the AMERICAN CHEMICAL SOCIETY were drawn up to be submitted to the Committee on Public Policy for their approval, which was granted unanimously. The Committee sought and finally obtained a hearing before the Committee on the Judiciary of the House of Representatives, to whom bill H. R. 5033 had been referred. [The resolutions of the SOCIETY which were presented to the Committee on the Judiciary at a special hearing were printed in THIS JOURNAL, **13** (1921), 570.]

Strong representations were made by us to the Committee on the Judiciary that nothing should be done to hamper or restrict the nonbeverage use of alcohol in the industries. Our Committee received able assistance at this hearing from Secretary Parsons and other members of the SOCIETY and took advantage of the services of representatives of industries having allied interests.

Because of the strong and valid objections raised against bill H. R. 5033 it was withdrawn by the Committee on the Judiciary, it having become apparent that it would not be easy to pass it. On June 1 they substituted in its place a new bill, H. R. 6752, which though less objectionable than the first would nevertheless have put unnecessary burdens and restrictions on industries depending on alcohol. An attempt was made to pass this bill without hearings or chance of offering valid objections. The request for summary action on this bill caused it to be referred to the House Committee on Rules. This committee granted us a hearing, and after considering our objections and those of other opponents of the bill, agreed with our contention that the bill if passed would have been unconstitutional and they refused to grant the special rule in its favor. A new bill, H. R. 7294, was then introduced, practically free from features objectionable to the industries, but the author of the former bills succeeded on the floor of the House in amending it in a manner that made it objectionable.

During all this time strong influences that were unmindful and inconsiderate of the rights and needs of industries were seeking through quick moves and irregular procedure to advance their special interests and where possible they sought to avoid public hearings that would give an opportunity for voicing valid objections. This made it necessary for our Committee to be ever on the alert. We were frequently put in the position where it was necessary to decide quickly and act without delay. Our position might have been likened to the man who, seeing the start of a fire, grabbed a pail of water and put it out, instead of letting the building burn down while seeking to learn if he was authorized to take the steps he did.

Bill H. R. 7294 which was originally introduced to prevent the prescription of beer for medicinal purposes was at first amended in a manner that was somewhat inimical to the industrial users of alcohol. It was later amended in the Senate so that when it finally became a law in November 1921 it was not hostile to industrial alcohol.

We have not considered the merits of prohibition as a committee, either for or against. The eighteenth amendment is very specific in its purpose and in the authority which it grants, and the National Prohibition Act expressly states that it is "an Act to prohibit intoxicating beverages, and to regulate the manufacture, production, use, and sale of high-proof spirits for other than beverage purposes, and to insure an ample supply of alcohol and promote its use in scientific research and in the development of fuel, dye, and other lawful industries."

This being the intent of the Constitution and of existing law, the Committee on Industrial Alcohol has felt that its duties were clearly defined. If we were to be of any use as a committee we could not sit idly by and see unnecessary and burdensome restrictions put upon the industries. This is a matter that we refused to compromise on. We were either right or wrong and we have used every effort to be on the side of right, and not to take sides in any doubtful matter.

Some of the legislation which was strongly urged would have put industries at the mercy of one man who would have been clothed at the same time with powers legislative, executive, and judicial. The manufacturer was put in the position that his business depending on the legitimate use of alcohol might be absolutely destroyed. A mere refusal to act, or neglect on the part of the Commissioner, would have sufficed to accomplish this result.

Industry is not responsible for the diversion of alcohol to illegitimate purposes and it has been repeatedly brought out that most violations have been due to the promiscuous granting of permits, and in many cases to corruption in the ranks of prohibition enforcement officers and to a neglect to carry out existing law.

We are credibly informed that a very general sentiment has been established in the minds of congressmen, largely due to our efforts, that nothing shall be done to injure industry in advancing prohibition enforcement.

Failing at gaining absolute power over industries through legislation, certain over-zealous persons are suggesting and seeking at this very time to accomplish their aim through arbitrary regulations.

Our attitude has at all times been helpful to those who respect the law, and we realize that every violation of the National Prohibition Act makes it harder for those who are respecting the law.

Only recently we received a request from one of the leading officers of the Treasury Department interested in the control of alcohol and liquors to coöperate with them and to give suggestions that would lead to a better enforcement of the law, including that portion which provides for the use of alcohol in the industries. Our Committee has expressed a willingness so to coöperate.

In conclusion we wish to state that we believe there is good ground for the continuance of a Committee on Industrial Alcohol, we recommend that such a committee should be appointed for the coming year, and we believe that its members will have ample opportunity to be of service to the SOCIETY and to the country.

MARTIN H. ITTNER, *Chairman*

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COMMITTEE ON PRIESTLEY MEMORIAL FUND

The Committee now offers its final report. It wishes to extend sincere thanks to the very generous contributors who made possible the fund with which to procure a suitable portrait of Joseph Priestley and to guarantee the cost of the die to be used in casting the Priestley Medal.

The portrait, as is probably known to everyone, is placed in the National Museum at Washington.

The die for the Medal is in the hands of Dr. John E. Teeple, Treasurer of the SOCIETY, to whom all residual monies have been paid.

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To the Committee it seems important that a record should be had of all who participated in making these undertakings possible. The names of the donors are, therefore, submitted, the amounts of their several contributions being withheld.

Charles F. Chandler
Charles Baskerville
George F. Kunz
George J. Pickel
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Dean Marion Talbot
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Sowers Mfg. Co.
Herold China & Pottery Co.
Ralph E. Meyers
Otto Behrend
Gregory P. Baxter
C. A. Browne
Fred Rosengarten

The Committee would recommend to the Council the following rules to be observed in the award of the Priestley Medal:

1—The Medal shall be known as the Priestley Medal, and shall be awarded every three years for distinguished services to chemistry.

2—The Committee of Award shall consist of the President of the AMERICAN CHEMICAL SOCIETY, his immediate predecessor in office, the Secretary and Treasurer of the SOCIETY, and the Editors-in-Chief of the Journals of the SOCIETY.

3—The Medal may be awarded not only to members of the SOCIETY, but to nonmembers, and to representatives of any nation, without regard to sex.

4—The Medal shall not be awarded more than once to the same individual.

5—The recipient of the Priestley Medal may be invited to deliver an address at one of the general meetings of the AMERICAN CHEMICAL SOCIETY, as may be determined by the Committee of Award.

The Committee further recommends that the first award shall be made at the General Meeting of the AMERICAN CHEMICAL SOCIETY in September 1922.

EDGAR F. SMITH, *Chairman*

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REPORT OF COMMITTEE ON SUPERVISION OF CHEMICAL ENGINEERING CATALOG

The sixth edition of the *Chemical Engineering Catalog* was ready for distribution during the week of the Chemical Exposition in New York in September 1921. The book went forward systematically thereafter, the entire distribution being effected by January 1, 1922.

The introduction of a fee of $2.00 a year for the use of the *Catalog*, which was introduced in 1920, proved to be a very effective means of distributing the catalog, as it eliminated waste of copies and improved the character of the mailing list; it did not in any way diminish the demand for the *Catalog*.

Eleven thousand five hundred copies of the *Catalog* were sent out and a list has been printed, giving the name, address, and business connections of each recipient. This list is furnished to all the firms represented in the *Catalog* and its use is confined strictly to them.

In the 1921 edition there were 667 firms using space, and statistics show that there is an increasing tendency on the part of the space-users to contract for more space, in order to catalog their products properly. The total number of catalog pages in the 1921 edition is 971.

In order to lessen the weight of the book, which is becoming unwieldy, the publishers have produced it with a flexible leather cover and a much higher grade of thin paper, which makes a much improved edition.

We believe that there is a growth in the scientific value of the information given. The officers of the *Catalog* constantly refer copy of the proposed data and general information to the Committee for suggestions and criticism, and in many cases the publishers have refused profit by rejecting mere advertising and choosing, rather, more scientific copy.

The duty of the chemical engineer is to observe this particular feature and to do his share toward obtaining the desired results by encouraging space-users to present more detailed facts concerning their products.

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Your representative attended several informal meetings of the Committee and has had a large number of informal conferences with the officers and editor of the *Catalog* and has endeavored in every possible manner to be of assistance to these gentlemen in their activities. The informal meetings are usually called to discuss principally matters of policy, as we are often called upon to assist the officers in obtaining from the manufacturers the proper data and information.

The prospects for the 1922 edition of the *Catalog* are much better than they were for 1921, when the business depression was felt. A number of firms that withdrew their space in 1921 have again applied for space in the 1922 edition, and, as stated previously, the data submitted are constantly being improved.

E. R. WEIDLEIN, *Chairman*

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REPORT OF COMMITTEE ON GUARANTEED REAGENTS AND STANDARD APPARATUS

The Committee has continued the work on elimination of sizes and shapes of apparatus that was described last year. A second detailed report has been prepared for publication. In this report 520 items are retained out of a total of 1246 considered by the Committee.

Elimination has been attempted without going into the question of exact dimensions. It is hoped that further recommendations may be made as to dimensions of the items retained.

W. D. COLLINS, *Chairman*

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REPORT OF COMMITTEE ON STANDARD METHODS FOR THE EXAMINATION OF WATER AND SEWAGE

In coöperation with the Committee of the American Public Health Association, our Committee has completed a revision of the Standard Methods of Water Analysis, the final manuscript of which was forwarded last week to the proper authorities of the American Public Health Association for publication. When printed, it is our intention to submit a copy to the Secretary's office as a permanent record of our work.

The portions of the work assigned to members of the AMERICAN CHEMICAL SOCIETY Committee were as follows: definition of alkalinity and temporary hardness; methods for hydrogen-ion determination; methods for sewage testing; mineral analysis; standard specifications for Nessler tubes; turbidity.

It is my understanding that the title page of this revision will bear the usual inscription including the names of the coöperating societies.

The duties of the Committee for the next few months will be simply to read proof. It is therefore desirable that the present personnel be continued until the present edition is published.

A. M. BUSWELL, *Chairman*

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REPORT OF METRIC SYSTEM COMMITTEE

I have the honor to submit the following report for the Committee on Metric System to coöperate with the American Metric Association, the World Trade Club, and the London and Manchester Metric Associations. We have during the year published three papers on the use of the metric system in the *Journal of Industrial and Engineering Chemistry* and also one article in *Science*. As recommended by the Council, we have also written to the colleges and universities as well as many technical firms using chemicals, urging them to purchase their chemicals in metric units; some 325 colleges have responded definitely in the affirmative, one only being opposed. Some 250 technical firms have also signified their intention of purchasing chemicals and supplies as far as practical in metric units. This work has entailed a great deal of correspondence and we have written between 5000 and 10,000 letters during the year. In this work we have had financial assistance from our SOCIETY and from the American Metric Association.

The work which we had planned for the year entailed a much larger expenditure than the money at hand and rather than hold the work back the Committee has met the expense. We have worked out a program for making this work self-supporting. We have attempted to enrol those who were coöperating with us as members of the American Metric Association, and in return the A. M. A. has agreed to give us 90 per cent of the dues received. If our policy is followed there should in time be a considerable revenue from this resource.

We have distributed some 20,000 stickers [to be affixed to letters sent to manufacturers and dealers] and have had requests for more from several sources. Their use should bring about a considerable pressure upon those firms, such as the Grasselli Chemical Company, which refuse to supply goods in metric units.

We have presented the metric cause before several bodies, such as the American Physical Society and the American Naturalists, and we have plans for a large amount of work of this sort before scientific educational bodies. The meeting on world standardization in New York was well attended and produced good results. We desire to have another meeting in Pittsburgh of considerably larger scope. We would like to have the Council give us permission to invite representatives of all the principal scientific, medical, engineering, and educational societies to meet with us at Pittsburgh to consider what steps can be taken advantageously to further the gradual adoption of the metric system in America and to investigate what the cost of the transition to the metric system may be and how the transition may be effected with the least inconvenience to the community. The question of cost is the one which is always mentioned by the opponents of the metric system. It appears probable from our experience in regard to chemicals that the argument is largely without foundation. If we could speak on this matter authoritatively after investigation, it would do much to promote the object which we have in view. Doctors and pharmacists are using metric units to a slight extent. This can be greatly increased. Some of our correspondents have begun giving talks to different bodies on the subject. We should have committees in every state to appear before our educational, scientific, and civic associations to present the metric cause. It seems to me that here is an important opportunity for leadership for our great organization.

Eugene C. Bingham, *Chairman*

Meeting of Local Section Officials

A meeting of Local Section officials took place at 4 P.M. at the Tutwiler, with W. L. Lewis presiding. Mr. E. M. Billings of the Rochester Section acted as Secretary. The following subjects were discussed:

(1) Standardization of Section By-laws. A committee consisting of the chairman and secretary was appointed to study the present Section By-laws and recommend a uniform code embodying the best features in the experience of the several sections.

(2) Relations to the National Society. The desirability of discussing National Association issues in the Local Sections, instructing and informing council-men, educating the members as to the national organization, candidates for national offices, etc., were freely discussed.

(3) Section Programs. Under this caption such matters as securing national speakers, routing prominent chemists, keeping in each section a lot of available local speakers, etc., were discussed.

Other matters considered were permanent employment bureau management work in the Sections, financing the Sections, interesting the young members, what to do with the ladies, and the desirability of educating chemists and employers to clear for positions through the college professors.

About 30 representatives of the several Local Sections were present at the two-hour session of the Section. The interest manifested demonstrated the need of and possible service through open discussions of this character.

The Chairman reported at some length on the Chicago plan of group meetings held simultaneously following the general talk of the monthly program, recommending it for consideration by the other larger sections which had not already developed something of the kind. It was generally agreed after this informal discussion, which demonstrated the proper subjects for consideration, that at the next meeting more definite progress would be made by calling in advance for the preparation of papers along some of these specific lines above suggested.

W. L. Lewis, *Chairman*

NOTES AND CORRESPONDENCE

Utrecht Meeting

Editor of the Journal of Industrial and Engineering Chemistry:

The following formal invitation has been issued to a chemical meeting at Utrecht in June:

> Utrecht, March 1922
>
> Dear Colleague:
>
> In June of last year Professors Biilmann, Bruni, Ernst Cohen, Donnan, Victor Henri, Kruyt, van Romburgh, Schenk, Walden and Wegscheider met in conference at Utrecht, and agreed to hold there in 1922 a scientific chemical meeting, the date of which is now fixed for June 21, 22, and 23 of this year. The program will consist of several general papers, together with a number of shorter scientific communications.
>
> It would give us very great pleasure, dear Colleague, if you would take part in this meeting.
>
> Awaiting a reply at your earliest convenience, and with best wishes,
>
> Yours very truly,
>
> Ernst Cohen
> H. R. Kruyt
> P. van Romburgh

The following American chemists are already planning to attend the conference: Drs. Edward Bartow, W. R. Whitney, L. W. Dennis, and W. A. Noyes. Other names will probably be added to the list later.

W. A. Noyes

University of Illinois
Urbana, Ill.
March 25, 1922

Determination of Arsenic by the Distillation Method

Editor of the Journal of Industrial and Engineering Chemistry:

Messrs. J. J. T. Graham and C. M. Smith [This Journal, 14 (1922), 207] recommend hydrazine sulfate and sodium bromide in the determination of arsenic by the distillation method. Hydrazine sulfate and hydrobromic acid have been used by the writer in the laboratory of the Coniagas Reduction Co., since 1911, and about 10,000 determinations of arsenic in cobalt ores and metallurgical products have been made in the above laboratory by means of these reagents. The writer made 2 kilos of hydrazine sulfate by the elegant method of Raschig [*Ber.*, 40 (1907), 4587] during the latter part of the war, when this material could not be purchased on the open market. Among the many advantages of hydrazine sulfate over other reducing agents the writer would like to draw attention to the following points:

The introduction of large amounts of fixed salts which are liable to cause bumping during the latter stages of the distillation is avoided.

The residue from the distillation is readily available for the determination of other constituents after destroying the excess of the reagent with bromine water or hydrogen peroxide.

C. A. Knittel

45 Chaplin Ave.
St. Catharines, Ont., Canada
March 9, 1922

Some Difficulties of the Manufacturer in the United States

Editor of the Journal of Industrial and Engineering Chemistry:

The writer is technical director of the Chemisch-Pharmazeutische Fabrik ByCo., S. A., which was first organized in Los Angeles and later reorganized with increased capital in Mexico. Its products are at present standard pharmaceuticals, such as tablets, ointments, fluid extracts, etc. The manufacture of chemicals is to be taken up in the future.

I believe that there is something of general professional interest in a rather detailed account of the experience of this organization, when we struggled in vain against an ever-increasing, excessive, and extreme legislation, perhaps more pronounced in California than in any other state, which finally forced us to throw up our hands in despair and to transfer our plant to Mexico City.

In Los Angeles we conducted an analytical laboratory doing principally clinical work. Connected with the analytical laboratory was a manufacturing laboratory equipped with power machines for the manufacture of medicinal tablets, etc. Other products were cosmetics and pharmaceutical and chemical specialties. It was also planned to make flavoring extracts in collapsible tubes.

We were subjected to the following laws and permits required:

Prohibition laws, in the use of alcohol for industrial purposes, in the analytical laboratory, for cosmetic preparations, in the recovery of alcohol.

The details connected with the many intricacies of these laws, expenses, etc., referring to our plant I need not rehearse here. Suffice it to mention that the Federal office in Los Angeles refused to accept our application for the use of alcohol for certain medicinal tablets where it was essential to make the necessary granulation, without our submitting formulas and labels for such tablets, a procedure which was of course impossible because we could not foresee what formulas would be submitted to us to be made into tablets. That the alcohol was used solely as a binder and was entirely driven off on subsequent drying of the product did not change the solomonic dictum of the Federal office.

Narcotic laws, involving a permit to use narcotics for medicinal tablets, and another permit to analyze for customers preparations containing alkaloids (narcotics).

The study of the California state food and drug laws, those of the State Board of Pharmacy, Federal legislations, the filling out of the many application blanks, the monthly accounts required, the study of new amendments (added frequently) would almost require one man's time, a cost too great for a small plant.

At the time we left California, three bills were pending before the Legislature which would have added to our burden.

The first of these bills was the Economic Poison Law (disinfectants), which if passed would require a special permit to manufacture disinfectants and a yearly tax of $50 for the same, doubtless with another series of application blanks, etc.

The second referred to the labeling of flavoring extracts. According to what I have been told by a well-known color manufacturing house, the bill was intended to prohibit the use of pictorial reproductions of any fruit, as well as the names of fruits, on the label, provided the flavors were manufactured from synthetics.

The last of these bills would have been disastrous to our analytical laboratory because it would prohibit anyone but a registered physician from performing analyses of a clinical nature. An abstract of this bill was published about half a year ago in the *Journal of the American Pharmaceutical Association.*

The following species of the family of inspectors did honor us with their visits, or would have done so had we been able to obtain all the necessary permits for the manufacture of our goods (a special reception room would have been quite appropriate): boiler inspector, Board of Health inspector, safety inspector (machinery), prohibition inspector, corporation inspector, county tax assessor, scale inspector, Board of Pharmacy inspector, narcotic inspector, fire inspector, city license inspector, and *vivant sequentes.* The possible passing of the Economic Poison Law would probably have acquainted us with still another member of the family.

We do not care to express the feelings which we experienced when one of the boiler inspectors (we had a large upright gas boiler for the generation of live steam) inquired, "Which machine is the boiler," and "Is this a copper or iron boiler," and when patiently given the desired information proudly handed us his official notice, "Boiler inspected and found to be in good order."

There is a very marked contrast in the situation with which we were confronted when hopelessly striving against official meddling, and the freedom which we can enjoy in our business enterprise here in Mexico. Undoubtedly, a highly organized industrial nation will require a more complex system of legislation than a nation of less industrial development, but the grinding out of national and state legislation, passed and contemplated, should not come to a point where it becomes an oppression and an interference in rightful business, much intensified in times of already existing industrial depression.

The purpose of this letter is to enumerate the particular difficulties which we encountered in Los Angeles, which have forced us, in order to save our investments, to look for freedom in doing business for a place where we can recover our losses sustained through excessive legislation, and where we shall be able to do better than merely fill out numberless application blanks, pay taxes for permits, and obey the frequently arbitrary orders of frequently autocratic and ignorant inspectors.

C. Braubach

ByCo.
Chemisch-Pharmazeutische Fabrik, S. A.
Calle de Rosales 1
Mexico, D. F.
January 25, 1922

The Lime Fellowship of the Eastern Potash Corporation at New Jersey Agricultural Experimental Station

Occasionally in the solving of a research problem pertaining to the manufacture of chemicals, one must go to a field other than that embraced by the chemical laboratory or the semi-works plant. For example, in the manufacture of caustic potash and potassium nitrate from greensand, the Eastern Potash Corporation will obtain a large tonnage of a liming material containing approximately the same amount of CaO as is in ordinary limestone.

It was thought that this lime residue from potash extraction, which has been named limosil, would be applicable for the liming of soils. In order to test this possibility, research was transferred from the chemical laboratory to Nature's laboratory, and during the past year the New Jersey Agricultural Experiment Station at New Brunswick, under the direction of Dr. J. G. Lipman, has been investigating this problem in the greenhouses and also in the fields. The results to date indicate that this potash by-product is as efficient as limestone or slaked lime in the liming of acid soils, the comparison of course being made on the basis of an equal CaO content.

As a great area of the soils, especially of the eastern United States, are in need of lime, this new by-product should not only cheapen the manufacture of domestic potash but also increase the yield from our farms. In carrying out such field and greenhouse experiments, the aim has been to parallel the actual practical tests on growing plants with laboratory studies of the effect of the lime on the various constituents of the soils, with the object of some day knowing just how the lime functions.

R. Norris Shreve

New York N. Y

Determination of Salt in Petroleum

Editor of the Journal of Industrial and Engineering Chemistry:

In the January number of This Journal, 14 (1922), 80, Mr. George T. Dougherty calls attention to a method which was published under my name in an earlier number [13 (1921), 325], for the determination of salt present in oil. He outlines a method used by the American Steel Foundries in Chicago for the same purpose, and, in going over it, I find we used about the same method when we first started our efforts toward determination of the amount of salt in oil.

It did not seem that we found all the salt present, however, owing to the difficulty of getting a proper extraction of the salt from the charred material left after burning the oil. Also, if the oil contained much salt water there was some loss due to spattering, which could not be prevented.

This led to the development of the method using acetone for extraction, which has the advantage of working on a larger quantity of oil; while it takes a little longer, it apparently extracts the salt water more thoroughly, as indicated by the following results, which are expressed in grams of salt per liter of oil:

Determination of Salt in Crude Oil Sample

Method	Acetone	Burning
Test 1	0.70	0.51
Test 2	0.73	0.57

Determination of Salt in Fuel Oil Sample

Test 1	0.95	0.81
Test 2	0.93	0.75

Ralph R. Matthews

Roxana Petroleum Corporation
Wood River, Ill.
March 24, 1922

Chilean Nitrate

Editor of the Journal of Industrial and Engineering Chemistry:

The savants and pseudo-savants who attended the meeting of the British Association at Bristol in 1898 were hoodwinked by Louis de Rougemont's story of fictitious adventure in northwestern Australia and startled by the Crookes' warning, equally absurd, as to the early exhaustion of the nitrate beds in Chile. The repetition of the Crookes' prophecy, omitting dates of course, will serve doubtless as an inspiration to authors of chemical treatises for many years to come; during the intervening time the public will still be told that our supply of iodine comes from seaweed.

Recently, however, another phase of the subject has developed, and technical journals and the daily press have been making direct reference to the nitrate deposits in the extreme north of Chile, thus complicating the Tacna-Arica controversy between Chile and Peru. On page 218 of your March issue you refer to the "potentially valuable nitrate beds" there; and, later, to the fact that "government experts" maintain that the district contains "valuable nitrate beds." Statements such as these smack so strongly of propaganda against Chile that they should be examined carefully before publication. The commercial nitrate deposits are far to the south. There is no more reason to assume that "valuable nitrate beds" occur in Tacna and Arica than that similar resources will be developed in every other arid region in the world.

A. W. Allen

Berkeley, Cal.
March 15, 1922

In spite of a convincing demonstration last year that the by-product coking of bituminous coal could maintain itself better than could the beehive method in a period of industrial depression, and that by-product coking is continuing to supersede the older method, production of coke by-products during 1921 averaged in the neighborhood of one-third less than the 1920 output.

The Flow of Fluids through Commercial Pipe Lines—Correction

In the article under the above title [This Journal, 14 (1922), 105] the following errors should be noted:

Page 112, 1st col., 3rd line in next to last paragraph, correct "Fig. 9" to read "Fig. 10."

Page 115, 2nd col., Section 4, the second equation should be

$$p = \frac{0.0538\, f\, l\, s\, Q^2}{D^5}.$$

Page 119, 1st col., 1st line, the sentence should read "From Fig. 17, $s = 0.00118$, etc." instead of "$z = 0.00118$, etc."

R. E. Wilson
W. H. McAdams
M. Seltzer

Massachusetts Institute of Technology
Cambridge, Mass.
March 20, 1922

Solid Sodium Hydroxide as an Absorbent for Carbon Dioxide in Steel Analysis

Editor of the Journal of Industrial and Engineering Chemistry:

The paper of the above title by Messrs. G. L. Kelly and E. W. Evers in the November issue of This Journal treats a subject which is of supreme importance to the steel works chemist.

We feel it would interest other workers to know that independent investigators in Britain and America have established by their separate experience the practical advantages to be gained by the use of solid sodium hydroxide as an absorbent for carbon dioxide in the estimation of carbon.

It has been the standard practice since 1906 in the laboratories of Messrs. William Beardmore & Co., Ltd., Glasgow, to use solid sodium hydroxide as an absorbent in all carbon estimations. In this period a total approaching half a million estimations has been made and on this experience we can corroborate all the claims the authors put forward for the solid absorbent.

We have examined experimentally from time to time the proposals and claims made on behalf of apparatus and reagents both for liquid absorption and gaseous measurement and have found no sufficient reason to depart from our standard practice. This consists of the absorption of the carbon dioxide by the solid sodium hydroxide which is loosely packed in U-tubes with stoppers and side limbs.

The application of the use of soda asbestos noted in the authors' earlier paper [This Journal, 8 (1916), 1038] was most opportune for us as it aided us in overcoming a war-time difficulty, and at the time the very real difficulty, of replacing impure and mechanically imperfect soda lye. Unfortunately we had the moisture difficulties noted by Messrs. Kelly and Evers. We have tried the absorption apparatus sketched therein and have found it admirably suited for the work.

Jas. MacWhirter, F.I.C.
Chief Chemist

Laboratories of
Messrs. William Beardmore & Co. Ltd.
Ordnance & Steel Works
Glasgow, Scotland
January 26, 1922

Platinum Theft

On April 1 the laboratory of the Agricultural Experiment Station of the University of Florida lost by theft seven platinum evaporating dishes, average weight 18 to 21 grams, numbered as follows; 1, 2, 3, 11, 6, 7, 9.

R. M. Ruprecht

WASHINGTON NOTES

DYE INVESTIGATION

The dye investigation is practically over, and as each witness has completed his testimony the fact is more forcibly and increasingly impressed upon us that the domestic dye industry will be completely vindicated. Seven weeks have been consumed in the hearings, and thus far not one person who has testified before the committee has shown that any monopolistic tendency exists. Importers, manufacturers, and users of dyes have all appeared and each, in turn, has testified that there is no monopoly of any kind. Even the small producer has failed to appear and testify to the existence of a monopoly.

The second point that the committee was charged to investigate was the question of lobbying. There has been no testimony that there has been lobbying, nobody has defined lobbying, and apparently there has been no attempt to prove that there has been lobbying. Senator Shortridge has repeatedly announced that if anyone had any evidence or wished to ask any questions relative to lobbying or monopoly they were free to appear and question the witnesses or the committee. Yet no one has appeared to propound such questions.

THE INEVITABLE

The friends of the American potash industry have always taken the attitude that all that was necessary was to give any unbiased judge the facts about this infant American industry and he could not do otherwise than decide that the enactment of a protective tariff was the only hope for the industry. In this they were not mistaken, as is evidenced by the provisions contained in the Tariff Bill, which has been passed by the House, approved by the Senate Finance Committee, and favorably reported to the Senate, and which briefly is as follows:

> That for a period of 5 years beginning on the day following the passage of the Tariff Act, there shall be levied, collected, and paid, on the actual potash (potassium oxide) content of potassium, chloride or muriate of potash, potassium, kainite, wood ashes and beet-root ashes, and all crude potash salts not specially provided for, a duty of 2.5 cents per pound for the first two years; 2 cents per pound for the third year; 1.5 cents per pound for the fourth year; and 1 cent per pound for the fifth year: thereafter the said potash content shall be free of duty.
>
> Potassium nitrate, or crude saltpeter, is admitted free of duty.

MUSCLE SHOALS

The House Committee on Military Affairs has completed its hearings and has printed eleven volumes containing the testimony that was given before the committee. On March 25, 1922, members of the Senate Committee on Agriculture and members of the House Committee on Military Affairs left Washington on an inspection trip of the Muscle Shoals project. About ten members from each branch of Congress made the trip, a number of members being detained in Washington because of other activities. The party was gone a little over five days and in that time made a complete inspection of everything in the vicinity that was in any way connected with the Muscle Shoals Project.

The members returned to Washington fully realizing that the Muscle Shoals undertaking is one of the most important that has ever been undertaken in this country for the development of our natural power. The consensus of opinion, however, seems to be that Congress cannot accept or reject any proposition relative to the purchase of this project but the importance of completing the Wilson Dam is thoroughly understood and indications are that an appropriation will be made available for the completion of the dam by the Government pending a decision relative to the various proposals which have been made for Muscle Shoals. Meantime the Senate Committee on Agriculture started its hearings on Monday, April 10.

METRIC SYSTEM

Hearings on the metric system bill have been completed. There is a strong sentiment even among some manufacturers of the country for the enactment of this bill into law, but this is offset by strong opposition on the part of certain manufacturers and interests that have organized to prevent the measure being adopted. Neither has the coöperation of the government departments been secured, some of the cabinet officers having declined to endorse the bill because they thought its enactment would cause confusion and expense to the Government. In the face of so much opposition it is very doubtful if any favorable action will be taken in the near future.

BOARD TO ADMINISTER MEDICAL FELLOWSHIPS

The National Research Council has appointed a special Board of eminent medical men to administer the National Fellowships in Medicine which the Research Council is able to offer through special gifts to it by the Rockefeller Foundation and General Education Board amounting to $100,000 a year for five years.

The members of the Board are: Victor C. Vaughan, *Chairman*, David L. Edsall, Joseph Erlanger, G. Carl Huber, E. O. Jordan, Dean D. Lewis, W. G. MacCallum, Lafayette Mendel, and W. W. Palmer.

The fellowships are open only to students who have already obtained the degree of M.D. or Ph.D. or have equivalent qualifications. Fellows will be appointed for one year with the privilege of applying for reappointment. Applications or requests for special information should be made to the Division of Medical Sciences, National Research Council, 1701 Massachusetts Ave., Washington, D. C.

KELP POTASH PLANT SOLD

The Kelp Potash Plant of the Bureau of Soils, U. S. Department of Agriculture, at Summerland, Cal., was sold and transferred on April 1 to Mr. Rodney Benson of Santa Barbara. The plant will be enlarged and put back into operation at once for the manufacture of "kelpchar" (a decolorizing carbon of very high activity), potash salts, and iodine.

LIME SPECIFICATIONS AND METHODS OF SAMPLING AND ANALYSIS

A meeting of Committee C-7 of the American Society for Testing Materials was held at the offices of the National Lime Association in Washington, D. C., on March 28 and 29. Specifications for sampling lime products, for determining the amount of available lime in quicklime and hydrated lime, together with specifications covering the use of lime in varnish manufacture, rag cooking, silica brick, sulfite pulp, and in the textile industry were presented to the whole committee for approval. These specifications will probably be presented to the Society at the annual convention for adoption as tentative standards. Considerable progress was reported by the subcommittees dealing with the use of lime in construction. The agricultural interests are working in conjunction with the American Association of Official Agricultural Chemists in an effort to develop standard methods of sampling and analysis.

New definitions of the terms quicklime and hydrated lime which are clear, concise, and complete, were adopted by the Committee, and careful study is being given to about one hundred other terms which are of special interest to this committee.

There will be a meeting of the Station Superintendents of the U. S. Bureau of Mines in Washington and Pittsburgh, the week of May 17. The meeting will be in Washington on Monday, Tuesday, and Wednesday, and in Pittsburgh on Thursday, Friday, and Saturday of that week. All of the Station Superintendents will be in attendance and the various problems with which they are confronted will be discussed at length.

Dr. R. B. Moore will leave on May 6 for a 2 months' trip abroad to carry out certain investigations for the Bureau of Mines.

The Bureau of Mines is arranging with a number of oil-producing companies in California to make motion picture films that will be useful in teaching the gospel of safety in the petroleum industry.

April 15, 1922

Personals

Dr. William A. Perlzweig, formerly research biochemist in the N. Y. branch of the Hygienic Laboratory, has accepted the position of chemist to the Medical Clinic in the Johns Hopkins University.

Dr. Lester A. Pratt, who has been in charge of the Research Laboratory of the Merrimac Chemical Co. for the past six years, has been made director of research for the same company.

Mr. E. M. Partridge, formerly chief chemist of the Refinite Co., Omaha, Neb., is now chemist for the Paige & Jones Chemical Co., Hammond, Ind.

Mr. Henry G. Knight, formerly dean of agriculture of the Oklahoma Agricultural and Mechanical College and director of the Experiment Station, has been elected director and research chemist of the W. Va. Agricultural Experiment Station of the University of West Virginia. In November Mr. Knight was elected Honorary Fellow of Cornell University.

Mr. Frank E. Swindells left the employ of the Standard Chemical Co. on November 1, 1921, and joined the staff of the Bureau of Standards.

Mr. W. F. Washburn has resigned his position as assistant general manager of the Titan Co. A–S of Fredriksstad, Norway, and is now consulting engineer to the Titanium Pigment Co., Inc., Niagara Falls, N. Y.

Mr. John M. Grove, formerly connected with the Lee Tire & Rubber Co., of Conshohocken, Pa., and later with the N. J. Carspring & Rubber Co., Inc., of Jersey City, is now in charge of the laboratory of the New England Tire & Rubber Co., Holyoke, Mass.

Mr. Wm. C. McIntire has left the employ of the Cincinnati Chemical Works, Inc., and is now with the Sherwin-Williams Co., Chicago, Ill.

Mr. Wm. J. Burgess has resigned his position with the Electric Storage Battery Co., Philadelphia, to accept the position of chemical director of the Pennsylvania Coal Products Company's plant at Petrolia, Pa.

Mr. I. J. Jenks has accepted a position as professor of chemistry at the Northern Illinois State Teachers College, Dekalb, Ill. He previously occupied the position of chemist for the Brunswick Balke Collender Co., Muskegon, Mich.

Mr. Sam Tour, for a number of years metallurgist with the Technical Staff Office of the Chief of Ordnance, War Dept., Washington, D. C., is now with the Doehler Die Casting Co., Brooklyn, N. Y., in the same capacity.

Mr. Carl E. Hartwig, until recently associate chemist at Edgewood Arsenal, has accepted the position of research and development chemist with the Garfield Worsted Mills, at Garfield, N. J.

Mr. Walter S. Long has left the University of Kansas, where he was an assistant professor of chemistry, having in charge the work of the State Food Laboratory, to accept the position of City Chemist at Kansas City.

Mr. Chas. Braubach is technical director of the laboratories of the recently formed Chemisch-Pharmazeutische Fabrik ByCo. S. A., Calle de Rosales 1, Mexico D. F., of which company he is one of the founders.

Mr. H. G. Tanner has resigned his position as chief chemist of the U. S. Experimental Kelp-Potash Plant, Summerland, Cal., to assume the position of assistant professor in the department of chemistry, University of Oregon.

Mr. William C. Carnell died in Philadelphia on March 12, 1922, at the age of fifty-three. Mr. Carnell had been a member of the AMERICAN CHEMICAL SOCIETY since 1895, and had served on the Council and on various committees. He was very active in the Philadelphia Section, where his loss will be greatly felt. Mr. Carnell was a graduate of Lehigh University. Most of his professional career was spent in Philadelphia, in the field of acids and heavy chemicals. He became associated with Charles Lennig & Company in 1901, went to the Harrison Works, manufacturing heavy chemicals, pigments and paints, in 1913, returning to the Lennig Company in 1917. From May 1917 to August 1920 he was connected with the Rohm & Haas Co., after which time he again returned to Charles Lennig & Co.

Industrials

Mr. Robert C. Stanley, formerly First Vice President, was recently elected President of The International Nickel Company. Mr. Stanley has ordered a reorganization of personnel, involving as its chief feature a new department of Development and Research with headquarters at 67 Wall St., New York City.

The new department of the company is the outgrowth of a gradually maturing conviction that a study of its products and their successful use in the hands of the consumer is the key to the extension of tonnage distribution. Research departments at the mines, smelters, and refineries of the company, established during the last few years, have now been crystallized into a headquarters organization in intimate touch both with its own plant developments and with outside engineering developments, touching on the use of nickel and monel metal in all fields. This department will be under the direction of Mr. A. J. Wadhams, as Manager. Associated with him will be Dr. Paul D. Merica, Director of Research.

Mr. Wadhams has hitherto been manager of the large Bayonne refinery of this company and has for years been in direct charge of the manufacture of all of the company's products, and through this experience is fitted to an unusual degree for the new work which he is to undertake.

The Celite Products Company has recently established branch offices in Boston, Buffalo, Cincinnati, and Minneapolis, with the idea of securing increased business through direct concentrated effort.

The Combustion Engineering Corporation has recently opened a new branch office in Cleveland, Ohio, in charge of Mr. Frank Henderson.

The Freeport Sulphur Co., New York and Freeport, Texas, awarded contract on March 24 to Dwight P. Robinson & Co. for the design and construction of a complete sulfur mining plant at Hoskins Mound, Texas. The company now operates a large sulfur mining plant at Freeport, which contains one of the largest installations of oil-burning boilers in the world.

The Sarco Co., Inc., of New York has recently issued a bulletin—Sarco Temperature Control—illustrating various types of temperature regulators and their application.

The Century Wood Preserving Company has recently issued *Bulletin* 20, "Storing and Seasoning Cross Ties," which gives an interesting discussion of the methods used by the company, factors influencing seasoning, possible deterioration during seasoning, and methods of handling and storing.

Twenty-five companies were organized during the month of March to engage in the manufacture and distribution of chemicals, drugs, and dyes. The aggregate indicated investment was $12,625,000, as compared with an aggregate of $5,200,000 in February. The average investment per company organized was $505,000 in March, and $236,363 in February. Three companies were organized with an indicated investment of $1,000,000 or more during the month.

At the annual meeting of the Refractories Manufacturers' Association recently held in Chicago, the president urged the formation of a committee of thirteen to make a thorough industrial survey of operations in which refractories are utilized, to ascertain actual service conditions in the following fields: blast furnaces, not blast stoves; open hearth furnaces, soaking pits; heating, puddling and forging furnaces; all types of boilers; cement, lime and plaster kilns; window, plate, bottle and optical glass; annealing, malleableizing and air furnaces; water and coal-gas generators, gas producers; cupolas and gray iron furnaces; oil refineries; zinc, lead, and copper smelters; all types of by-product coke ovens; and all types of ceramic kilns.

Printed copies of patents may be obtained as follows: American, from the Commissioner of Patents, Washington, D. C., 10 cents each; Austrian, from Lehmann & Wentzel, Kaernthnerstrasse, 30, Vienna, 1, 20 cents each; British, from the Comptroller General, Patent Office, 25 Southampton Buildings, London, W. C. 2, 1 shilling each (plus 1d. postage); Canadian, manuscript copies only are available, estimates furnished in advance by Fetherstonhaugh & Smart, 50 Queen St., Ottawa; French, from l'Imprimerie Nationale, 87 Rue de Vielle de Temple, Paris, 1 franc each; German, from Reichspattentamt, Berlin, 5 marks each (lots of 20 or more, 2½ marks each).

BOOK REVIEWS

Benzine and Mineral Lubricants. By J. Formanek (translated from the German by Charles Salter). Cloth, $8^1/_2 \times 5^1/_2$. xii + 256 pp., 20 illustrations. Scott, Greenwood & Son, London; D. Van Nostrand Co., New York, 1921. Price, $5.00.

In this book, Formanek, who is a professor at the Bohemian Technical High School at Prague, considers the production, testing, and uses of gasoline, benzene, and petroleum lubricating oils. It embodies his experience as a motorist and a petroleum-products analyst, and it is intended for the guidance of users and testers of motor fuels.

There are 14 chapters, as follows:

Introductory
Petroleum: Its Composition and Treatment
Coal Tar Products
Brown-Coal, Shale and Peat-Tar Products
Products from Petroleum and Tar Residues
Testing Benzine and Benzene
Judging the Quality of Benzine and Benzene
Testing Mineral Lubricating Oils
Judging Mineral Lubricating Oils
Properties and Uses of Fuels
The Consumption and Efficiency of Various Fuels in Internal Combustion Engines
Suggested Improvements in Motor-Car Equipment
Safe Storage of Benzine and Benzene
First Aid in Cases of Gassing with Benzine

In discussing these various subjects, the author presents brief but informative descriptions of European and especially continental practice, but he has not accorded attention to American procedures. While the work will be of little value to the American petroleum chemist, the automotive engineer may wish to have it for reference, in order to have available the methods used in continental Europe for ascertaining the practical suitability of the materials currently employed for operating gasoline engines.

W. A. Hamor

Some Phases of Cost Accounting in the Chemical Industry. By C. B. E. Rosén, M. B. A., C. P. A. 18 pp. National Association of Cost Accountants, Bush Terminal Bldg., New York, 1921. Price, $0.75.

Mr. Rosén is evidently familiar with his subject and has brought his knowledge of accounting to bear on one of the most difficult problems in a field which has not been covered and in which no standard practice has been established.

More stress could be laid on Mr. Rosén's suggestion that a monthly determination of costs is apt to be misleading. If the costs for a three months' period are determined the conclusions reached are certain to be more accurate. This, of course, does not mean that detailed monthly costs should not be kept, but the conclusions drawn should be in the light of the three months' average.

The proper place for the deduction of by-products from the cost is a much mooted question, and the reviewer is rather inclined to differ with the author in this matter. Although it does not affect the costs whether deducted from raw materials or total manufacturing costs, it appears to the writer more logical that it should be deducted from the latter.

Mr. Rosén has laid stress on the item of repairs in chemical plants but he does not draw the line where repairs end and depreciation begins. It would seem that this is rather essential in setting up a reserve for both items so as not to confuse the repairs which are charged to conversion costs and depreciation which is charged to overhead. If the apparatus is to be kept in good condition by the repairs reserve, should there be so large an item set up as "10 to 20 per cent or more" for depreciation? Again, abnormally large discrepancies in "production reports" may eventually be charged off to profit and loss as suggested by the author but under no consideration should this be done until brought to the attention of the proper executive, for besides determining the costs one of the most essential reasons for the establishment of a cost accounting system is for the purpose of calling attention to just such discrepancies.

The items of cost are well considered but the detail of applying a cost accounting system to a chemical industry must be carefully studied; otherwise it will tend toward an elaborate and extensive collection of data which may be of little practical use when compiled.

Mr. Rosén's article is not a primer by any means, but presupposes a knowledge of cost accounting and might frighten the ordinary manufacturer. The latter should bear in mind that a knowledge of costs is the *sine qua non* of every successful business and that a vast majority of the failures of the country are brought about through the lack of knowledge of this essential requirement. Cost accounting is just as necessary to the chemical industry as to the shoe trade. A proper cost system is the guide to the conduct of a business and the details obtained in the collection of cost data are invaluable indications as to the trend of the business. They point out the cause of direct losses and draw attention to the efficiency or lack of efficiency in the various departments.

Mr. Rosén's pamphlet is a valuable contribution not only to the cost accountant but also to the chemical manufacturer.

William W. Caswell

Technical Records of Explosives Supply. 1915-1918. V—Manufacture of Sulfuric Acid by Contact Process. 128 pp., 43 figs. Ministry of Munitions and Department of Scientific and Industrial Research, London. H. M. Stationery Office, 1921. 19 × 28 cm. £1 5s. net.

Only the Mannheim and Grillo processes are treated of, 45 pages and 10 figures being devoted to the first, while 83 pages and 33 figures are assigned to the last-mentioned process. In the Mannheim plants iron pyrites was used as the source of sulfur. In the Grillo plants sulfur itself was burned to SO_2 on the ground that it required less skill to burn sulfur *per se* than to burn the sulfur out of pyrites and that, too, there was a saving in freight. The "lump" burners were of the usual type employed in England enclosed in sets of three with a flue in common and operated with dried air under slight pressure, but for "fines" Herreschoff burners were used. A small "lump" burner was erected beside each Herreschoff, the hot gas from which commingled in a common flue with the colder gas from the Herreschoff and brought the temperature of the mixture up to the optimum condition for oxide conversion. Careful precautions were used to prevent poisoning of the contact mass; yet when sulfur only, of high purity, was used it was found that the mass might suffer poisoning from arsenic picked up from the iron used in the construction of the plant. As in the previous works in this series[1] the apparatus and operations are described in minutest detail while quantities and yields are given. Of special interest is the preparation of the contact masses, both on the asbestos mat and the magnesium sulfate granule, as well as the recovery of the magnesium sulfate and platinum, together with the separation of platinum and iridium, from spent contact mass. No mention is made of the production of indurated refractory masses such as

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[1] See This Journal, **13** (1921), 1176; **14** (1922), 250.

were produced in this country in the use of a magnesium sulfate foundation. This volume maintains the high standard of its predecessors in the series.

CHARLES E. MUNROE

Technical Records of Explosives Supply. 1915-1918. VI—Synthetic Phenol and Picric Acid. 97 pp., 50 figs. 19 × 28 cm. Ministry of Munitions and Department of Scientific and Industrial Research, London. H. M. Stationery Office, 1921. Price, 15s. net.

Some 38 pages with 26 figures are devoted to phenol, while 59 pages with 24 figures are assigned to picric acid, the figures including photographs, graphs, and folded plates. The topics, as presented, afford excellent examples of the versatility of chemistry, both as to the variety of the raw materials that may be used and the many different processes that may be followed. Thus four methods of producing phenol from benzene and three from cresols are given, as well as eight different methods for making phenolsulfonic acid. The records show careful study of operating conditions, though, as these manufactures were carried out chiefly by private firms, they were much less under direct control of the Department than those which have been dealt with in previous records of this series.[1] Hence American practice is drawn upon in this report and commended. Recalling that before the War the Ordnance Department, U. S. A., required picric acid to be made from synthetic phenol, we read here, "For the production of picric acid no material difference between coal-tar phenol and synthetic phenol has shown itself either in the laboratory or on the large scale" but some impurities, such as paraffin, appeared to act favorably, as a catalyst. An example of the difference in products following the attempt to convert laboratory experiments into large-scale operations is given on page 47 in the recovery of the nitrogen products of nitration. The average yield of picric acid for these factories was 70.6 per cent of the theory. The most efficient working results were 76.6 per cent. Embarrassment resulted from the fact that rejected picric acid could be sold to manufacturers of sulfur dyes at a higher price than the Government paid for that meeting its specifications. This publication seems not to have had the careful supervision which characterized the previous "Records." Instances of dropped letters and numbers and of misspelled words occur, while in cases such as "explosions," on page 56, "nitration process," on page 64, and "sifting," on page 64, one is left in doubt as to what the author sought to say. Nevertheless the book is a valuable one and will hold its place as an authority.

CHARLES E. MUNROE

Harze, Kunstharze, Firnisse, und Lacke. By HANS WOLFF, PH.D. 115 pp. Verein Wissenschaftlicher Verleger, Berlin, 1921. Price 25 cents.

This little volume represents a successful attempt at printing, in pocket size, the essential facts concerning resins, artificial resins, varnishes, and lacquers. At a time when many authors are trying to dilute the known facts into many paged volumes, concise publications such as this are quite welcome. In any case the specialist will still consult the source books, such as those by Tschirch, Dietrich, and Seeligmann.

Dr. Wolff discusses the occurrence of the balsams and resins in certain organs of plants; Tschirch's chemical classification of resins; chemical and physical methods of testing resins. In Chapter 2, the author discusses the composition, chemical tests for, and uses of: seven balsams; three resinotannol-resins (acaroid, benzoin, dragonsblood); three resene-resins (elemi, mastic, dammar); four resinol-acid resins; a resinol resin (guaiacum); the aliphato-resins; the gluco-resins; eight different gum resins; the lacto-resins; and the enzymo-resins. Five pages are devoted to the artificial resins—cumarone and "formolite" (phenol-formaldehyde condensation products).

Part II covers 33 pages devoted to varnishes and lacquers, driers, solvents, linseed-oil-varnishes, stand oil (or lithographic oil), oil lacquers, volatile lacquers, water lacquers, sealing wax, and the testing of varnishes and lacquers. Twelve pages are devoted to tables showing properties of the acids of the principal resins, the resinic acids of various turpentines, the ester resins, the gum resins, solubility, acid and saponification numbers of the balsams and resins, and the properties of twenty common solvents. The articles on cellulose acetate lacquers and cumarone resins will be of interest to many who are interested in protective coatings and waterproofing agents. The booklet is printed in clean-cut Roman type and is supplied with a good index. The work of the author as court expert for the Chamber of Commerce in Berlin is a guarantee of the authoritative character of the text. Chemists desiring a concise review of the resin and varnish industry will do well to procure the booklet for perusal.

FREDERIC DANNERTH

Patents and Chemical Research. By H. E. POTTS. 198 pp. University Press of Liverpool, 1921. Price, 8s. 6d.

This is an able presentation in condensed form of the elementary principles of English patent law in the language of the chemist-layman.

The author is an experienced English patent agent and he addresses himself primarily to the director of industrial chemical research and to the manager of the chemical manufacturing plant. The impelling purpose of the book is stated in the preface as follows:

> Therefore it is most desirable that chemists should familiarize themselves with the leading principles of patent law; first, to enable them to coöperate with the patent agent and thus contribute to the object of obtaining secure protection for their inventions, and, second, so that their criticism will stimulate patent agents to maintain the highest level of professional skill. In this way, better work will be done, and the greatest benefits will be derived from the patent system.

Throughout the text, hypothetical as well as actual chemical cases are freely used with remarkable success for purposes of illustration. The first chapter is entitled "Patents as an Element of Business Policy," and deals especially with the relative advantages of patenting as against secret working as a means of protecting valuable chemical processes under the English law. The remaining chapters, except the last, deal with the cardinal principles of the English patent system. The last chapter treats briefly of the patent systems of other countries.

The book is well indexed but one might wish for more clearly marked subdivisions of the subject matter of the different chapters. There is a special index of cases, and subject titles of many of these cases are given in chemical terms—a distinct help to the chemist-reader.

The exposition primarily concerns the English patent system rather than that of the United States, and although many fundamental concepts are common to both systems it may not be amiss to caution the American chemist-reader against applying too directly in this country conclusions derived from a study of this book alone. The chapter entitled "Patents in Other Countries" will be helpful in indicating the numerous possible pitfalls in this direction.

In the opinion of the reviewer no single publication in recent years has greater potentialities for increasing the real effectiveness of systematic industrial research than the appearance of this book. A corresponding book dealing primarily with the United States patent system is greatly to be desired.

A. S. MCDANIEL

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[1] THIS JOURNAL, **13** (1921), 1176; **14** (1922), 250.

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

Chile still awaits a betterment in the **nitrate** trade of Europe and the United States. The prices on nitrate which were fixed on October 27, 1921, terminate on June 30, 1922, and lower prices are anticipated thereafter. (P. 546)

The year 1921 was marked by an exceedingly acute depression in the **iron ore** mining industry of Vizcaya, Spain, the chief source of wealth of that district. (Pp. 569–70)

In order to direct intelligently the work of searching for **petroleum** in Australia and New Guinea, the State Minister of Mines for New South Wales has announced that the State Government of that territory will assist the prospectors by advice and by subsidizing operations conducted at approved sites. (P. 573)

The quantity of **shale oil** produced in Australia during the year ending June 30, 1920, was 1,539,438 gal., and for the succeeding fiscal year, 2,612,976 gal. Shale deposits are found in numerous places in New South Wales, and it is asserted by the minister of mines for that territory that these deposits are the richest in the world. It is further stated that there is enough petrol in two of the sections alone to keep Australia for years absolutely independent of the outside world market if the present methods of extracting oil from the shale prove successful. (P. 573)

The **oil** industry in Poland has recently undergone a beneficial change because government restrictions have been very largely abandoned in favor of free trade, both for domestic and export business. The Bureau of Foreign and Domestic Commerce has on file statistics showing domestic and foreign deliveries of Polish oil in 1920. (P. 573)

The **petroleum** fields of Mendoza-Neuquen are described. (Pp. 573–4)

The Bureau of Foreign and Domestic Commerce has on file a report from Consul Henry D. Baker relative to the occurrence of **oil** in Trinidad. (P. 574)

Beginning with January 1, 1922, the use of the **metric system** of weights and measures is required in Lithuanian commercial and industrial establishments. (P. 590)

An account of the working of the **phosphate** deposits of Nauru and Ocean Islands has just been published in a report by the British senior trade commissioner of Australia. (P. 594)

A possible market for chemical **fertilizers** is reported in Indo-China. (P. 594)

Details in regard to the effect on the Scotch textile industries of the British **embargo** now placed on foreign **dyestuffs** may be had upon application to the Textile Division of the Bureau of Foreign and Domestic Commerce. (P. 616)

During the first months of 1921 about half of the automobiles in Pernambuco were using **alcohol fuel**, but to-day 90 per cent of these vehicles have resumed the use of gasoline. The reasons for this decline in the use of alcohol fuel are given and it is claimed that in spite of this abandonment of alcohol as a motor fuel everyone in Pernambuco still believes that alcohol is the future automobile fuel and, furthermore, considers it a patriotic duty as well as an economy to use alcohol. (Pp. 621–2)

The United States **petroleum** export trade in 1921 is reviewed. The report includes charts giving graphic presentation of exports by months for the years 1920 and 1921, as well as tables giving statistics of exports for the same period. (Pp. 638–40)

A record **shallow well** has been drilled in the Tampico **oil** fields, the daily production of which is estimated at 60,000 bbls. (P. 640)

The exploration of Bolivian **oil** fields by Swedish and German geologists is announced, but it is probable that the extraction will not begin for several years owing to the difficult nature of the country. (P. 640)

The period for the sale of **saccharin** as a substitute for sugar in Italy has been extended to June 30, 1922. Saccharin imported under this provision is admitted free of duty. (P. 650)

The operation of the **copper** mines in Mexico will soon be resumed. (P. 654)

A mining company in China is prepared to supply metallurgical **manganese** to the extent of 40,000 tons per annum and chemical manganese in small tonnage, the composition of the various grades being guaranteed. Further information may be secured from the Far Eastern Division, Bureau of Foreign and Domestic Commerce. (P. 656)

The production of Alsatian **potash** during 1921 shows a considerable decrease as compared to 1920. (P. 660)

Statistics are given showing the production of **crude oil** in Rumania during 1920 and 1921. (Pp. 700–1)

Petroleum possibilities in the Cadiz, Spain, Consular District are announced. The officials are very hopeful of important developments, provided foreign companies can be sufficiently interested to explore the fields thoroughly. (P. 701)

The revised **Spanish tariff**, which went into effect February 16, 1922, contains important changes in duties on the following American products: scientific apparatus; chemicals, including aniline oils, caustic soda and caustic potash, slag, superphosphate of lime; dyes and dyestuffs, coal tar; and petroleum products. (Pp. 712–3)

Certain **Italian export** restrictions have been removed on ingots of gold and silver containing platinum, mineral oils including petroleum, benzine, and charcoal. (P. 714)

Preparations are under way for the exploitation on a large scale of the **potash** deposits near Suria, Spain. It is believed that agriculture will be given a great impetus by the development of these potash deposits. (P. 723)

The value of **mineral production** in Canada in 1921 was $170,000,000 as compared with $227,859,665 in 1920. (P. 724)

Bleached pulp for the manufacture of newsprint which is being made in New South Wales has been officially inspected and approved. The pulp is made from the mountain gum tree, of which immense tracts are available. (P. 762)

Regulations relative to carrying out provisions of the Ecuadorean law relative to **petroleum** concessions may be consulted in the Bureau of Foreign and Domestic Commerce. (P. 762)

The Fuel Division of the Bureau of Foreign and Domestic Commerce has on file a statement that an electrochemical process has been perfected for the manufacture of metallic **calcium** and of 97.5 per cent **caustic soda**, free from chloride of soda. It is claimed for the process that it is much cheaper than others now in use. (P. 763)

Important changes in **import duties** affecting the following American products are imposed by the revised New Zealand tariff: calcium carbide; cottonseed oil; linseed (bulk); benzene; gasoline; kerosene; crude petroleum; paints, and colors. (Pp. 778–81)

Statistics are given relative to the **gum arabic** trade of the Sudan. (P. 786)

SPECIAL SUPPLEMENTS ISSUED

BRAZIL
BRITISH WEST INDIES
PORTUGAL
SPAIN
UNITED KINGDOM
  BRADFORD
Trade of FRENCH WEST AFRICA for 1920
  SENEGAL
  DAHOMEY
  FRENCH GUINEA
Trade of STRAITS SETTLEMENTS for 1920
Trade of TURKEY for 1920
TRINIDAD and TOBAGO

STATISTICS OF EXPORTS TO THE UNITED STATES

BRAZIL AND PERU—(P. 571)
Rubber
CEYLON—(P. 594)
Rubber
TUNIS—(P. 591)
Marjoram
Olive oil
ARGENTINE—(P. 652)
Linseed
CAIRO—(P. 786)
Gum arabic
Oil, crude, fusel

CURRENT PUBLICATIONS

NEW BOOKS

Clinical Diagnosis: A Textbook of Clinical Chemistry for Medical Students, Laboratory Workers, and Practitioners of Medicine. Charles Phillips Emerson. 5th edition, rewritten. 726 pp. Price, $7 50. J. B. Lippincott Co., Philadelphia.

Coal: Its Properties, Analysis, Classification, Geology, Extraction, Uses and Distribution. Elwood S. Moore. 462 pp. 142 figures. Price, $5.00. John Wiley & Sons, Inc., New York.

Colloid Chemistry of the Proteins. Part I. Wolfgang Pauli. Translated by P. C. L. Thorne. 140 pp. Price, 8s. 6d. J. & A. Churchill, London.

Combustion: The Chemistry of Combustion. J. Newton Friend. 110 pp. Price, 4s. net. Gurney & Jackson, London.

Dictionary: Dictionnaire Anglais-Français-Allemand de Mots et Locutions Intêressant la Physique et la Chimie. T. Cornubert. 300 pp. Price, 47fr. Dunod, Paris.

Electrodynamics: An Introduction to Electrodynamics from the Standpoint of the Electron Theory. Leigh Page. 134 pp. Illustrated. Price, $2.00. Ginn & Co., Boston.

Engineering Drawing: An Introduction to Engineering Drawing. J. Duncan. 158 pp. Illustrated. Price, $1.40. The Macmillan Co. New York

Explosives: Technical Records of Explosives Supply, 1915–1918. No. 5. Manufacture of Sulfuric Acid by Contact Process. 128 pp. Illustrated. Price, 26s. **No. 8. Solvent Recovery.** 22 pp. Price, 3s. 3d. Ministry of Munitions and Department of Scientific and Industrial Research. H. M. Stationery Office, London.

Fire Assaying: A Textbook of Fire Assaying. Edward E. Bugbee. 254 pp. 51 figures. Price, $3.00 net. John Wiley & Sons, Inc., New York.

Fuel and Lubricating Oils for Diesel Engines. W. Schenker. 126 pp. Price, $3.00. D. Van Nostrand Co., New York.

Fuel and Refractory Materials. A. H. Sexton and W B. Davidson. New edition, revised and enlarged. Illustrated. 382 pp. Price, $4.00. D. Van Nostrand Co., New York.

Gas: The Distribution of Gas. Walter Hole. 4th edition, rewritten and enlarged. 699 pp. Illustrated. Price,. 50s. net. Benn Bros., Ltd., London.

Gas: Messung Grosser Gasmengen. L. Litinsky. Chemical Technology Series, edited by A. Binz. 274 pp. Price, paper, 525 M, bound, 585 M. Otto Spamer, Leipzig.

Gas Chemists' Handbook. Compiled by Chemical Committee, Technical Section of American Gas Association. 2nd edition. 608 pp. Price, $6.00. American Gas Association, New York.

Geologie et Mineralogie Appliquées à l'Art de l'Ingenieur. L. de Launay. 418 pp. Price, 50 fr. J.-B. Bailliere et Fils, Paris.

Heat Conduction: Introduction to the Mathematical Theory of the Conduction of Heat in Solids. H. S. Carslaw. 2nd edition, revised. 268 pp. Illustrated. Price, $9.00. The Macmillan Co., New York.

Heating and Ventilation. John R. Allen and J. H. Walker. 2nd edition. 330 pp. Illustrated. Price, $3.50. McGraw-Hill Book Co., Inc., New York.

History of Chemistry: A Concise History of Chemistry. T. P. Hilditch. 2nd edition, revised. 276 pp. Price, 6s. Methuen & Co., Ltd., London.

Industry and Human Welfare. William L. Chenery. Price, $1.75. The Macmillan Co., New York.

Isotopes. F. W. Aston. 152 pp. Price, 9s. Edward Arnold & Co., London.

Liquid Fuel: Burning Liquid Fuel; A Practical Treatise on the Perfect Combustion of Oils and Tars, Giving Analysis, Calorific Values and Heating Temperatures of Various Gravities; with Information on the Design and Proper Installation of Equipment for All Classes of Service. William Newton Best. Revised and enlarged edition. 341 pp. Price, $5.00. U. P. C. Book Co., New York.

Medical Research Report: Report of the Medical Research Council for the Year 1920–21. 114 pp. Price, 3s. 6d. net. H. M. Stationery Office, London.

Metallography: An Introduction to the Study of Metallography and Macrography. Léon Guillet and A. Portevin. Translated by L. Taverner. 289 pp. Price, 30s. G. Bell & Sons, Ltd., London.

Oil Encyclopedia. Marcel Mitzakis. 551 pp. Price, 21s. Chapman & Hall, Ltd., London.

Oils: Chemical Technology and Analysis of Oils, Fats and Waxes. Julius Isidor Lewkowitsch. Edited by George H. Warburton. 6th edition, rewritten and enlarged. Price, $12.00. The Macmillan Co., New York.

Papier. G. Dalén. **Einzelschriften zur Chemischen Technologie.** Edited by Th. Weyl. Vol. I Pt. 1. 2nd edition. 122 pp. Price, 25 M. J. B. Barth, Leipzig.

Petroleum. A Treatise on the Geographical Distribution and Geological Occurrence of Petroleum and Natural Gas; the Physical and Chemical Properties, Production, and Refining of Petroleum and Ozokerite; the Characters and Uses, Testing, Transport and Storage of Petroleum Products, and the Legislative Enactments Relating Thereto, Together with a Description of the Shale-Oil and Allied Industries. Sir B. Redwood. 4th edition, revised and rewritten. 3 vols. 1383 pp. Illustrated. Price, set, $39.00. D. Van Nostrand Co., New York.

Physico-Chemical Problems Relating to the Soil. Report of General Discussion Held by the Faraday Society. 368 pp. Price, 10s. 6d. net. The Faraday Society, London.

Potash. Sydney J. Johnstone. New edition, revised and enlarged. 122 pp. Price, 6s net. John Murray, London.

Practical Physiological Chemistry: A Book Designed for Use in Courses in Practical Physiological Chemistry in Schools of Medicine and of Science. Philip Bovier Hawk. 7th edition, revised. 675 pp. Illustrated. Price, $5.00. P. Blakiston's Son & Co., Philadelphia.

Qualitative Analysis: An Outline of Qualitative Analysis of Inorganic Substances. Horace G. Byers. 227 pp. Price, $2.00. D. Van Nostrand Co., New York.

Rubber. Edith A. Brown. 88 pp. Illustrated. 2nd edition. Price, $1.50. The Macmillan Co., New York.

Soap-Making Manual. A Practical Handbook on the Raw Materials, Their Manipulation, Analysis and Control in the Modern Soap Plant. E. G. Thomssen. 251 pp. Illustrated. Price, $4.00. D. Van Nostrand Co., New York.

Turbines à Vapeur. M. Poincet. 336 pp. Illustrated. Price, 35 fr. J.-B. Baillière et Fils, Paris.

Universities and Scientific Life in the United States. Maurice Caullery. 286 pp. Price, $2.50. Harvard University Press, Cambridge.

Zirconium and Its Compounds. Francis P. Venable. A. C. S. Monograph Series. 173 pp. Price, $2.50. Chemical Catalog Co., Inc., New York

RECENT JOURNAL ARTICLES

Ammonia: The Oxidation of Ammonia. C. S. Imison and W. Russell. *Journal of the Society of Chemical Industry*, Vol. 41 (1922), No. 4, pp. 37*t*–45*t*.

Atoms and Isotopes. Ellwood Hendrick. *Chemical and Metallurgical Engineering*, Vol. 26 (1922), No. 13, pp. 583–87.

Cellulose: Problems of Cellulose Chemistry. Emil Heuser. *Paper*, Vol. 29 (1922), No. 23, pp. 7–10.

Clay: Suggested New Methods in the Preparation of Dust-Pressed Bodies. H. Spurrier. *Journal of the American Ceramic Society*, Vol. 5 (1922), No. 3, pp. 151–56

Coal: Bituminous Coal as Generator Fuel. W. A. Dunkley. *American Gas Journal*, Vol. 116 (1922), No. 11 (whole No. 3341), pp. 249–52, 260–61.

Coal: Neue Beiträge zur Enstehung und Chemischen Struktur der Kohle. Franz Fischer and Hans Schrader. *Brennstoff-Chemie*, Vol. 3 (1922), No 5, pp. 65–72.

Flue-Gases: Practical Interpretation of Automatically Recorded Volumetric Percentages of CO_2 in Flue-Gases. W. E. Appleby. *Chemical Engineering and Mining Review*, Vol. 14 (1922), No. 161, pp. 156–60.

Fluorspar in Open-Hearth Practice. S. Schleicher. *The Iron Age*, Vol. 109 (1922), No. 11, pp. 783–84. Translated from *Stahl und Eisen*.

Fuel: Causes and Prevention of Power and Fuel Wastes. H. D. Martin. *Color Trade Journal*, Vol. 10 (1922), No. 3, pp. 98–103.

Glass: Some Aspects of Science Applied to the Glass Industry. C. H. Kerr. *The Glass Industry*, Vol. 3 (1922), No. 4, pp. 69–71.

Glass: An Autoclave Test for the Grading of Chemical Glassware. W. L. Baillie and F. E. Wilson. *Journal of the Society of Chemical Industry*, Vol. 41 (1922), No. 4, pp. 45*t*–55*t*.

Iron and Steel Classified for Designers. William J. Merten. *Forging and Heat Treating*, Vol. 8 (1922), No. 3, pp. 155–60.

Iron: Researches on the Electrodeposition of Iron. W. E. Hughes. *Brass World*, Vol. 18 (1922), No. 3, pp. 80–85.

Metallurgy: The Correlation of Metallurgical Statistics. H. A White. *Journal of the Chemical, Metallurgical and Mining Society of South Africa*, Vol. 22 (1921), No. 6, pp. 97–106.

Monel Metal, A Natural Nonferrous Alloy. Morris A. Hall. *Brass World*, Vol. 18 (1922), No. 3, pp. 76–79.

Open-Hearth Furnaces: Design of Open-Hearth Furnaces. A. D. Williams. *The Iron Age*, Vol. 109 (1922), No. 9, p. 577; No. 11, p. 717; No. 13, pp. 853–55.

Sewage: Further Experiments with Activated Sludge. E. Hannaford Richards and G. C. Sawyer. *Journal of the Society of Chemical Industry*, Vol. 41 (1922), No. 5, pp. 62*t*–72*t*.

Steel: Influenza della Temperatura sulle Proprietà Meccaniche della Ghisa. F. Graziana. *Giornale di Chimica Industriale ed Applicata*, Vol. 4 (1922), No. 2, pp. 53–56.

Tanning: A Critical Study of the Determination of the Active Constituents of Synthetic Tanning Materials by the Hide Powder Method. S. Kohn, J. Breedis and E. Crede. *Journal of the American Leather Chemists Association*, Vol. 17 (1922), No. 4, pp. 166–80.

Tin: The Metallurgy of Tin. Walter H. Jacobson. *The Metal Industry*, Vol. 20 (1922), No. 3, pp. 103–5.

Water Resistant Glues: Casein and Blood Albumin. Robert Herman Bogue. *Chemical Age*, Vol. 30 (1922), No. 3, pp. 103–6.

Wood: Proper Use of Wood in Connection with Dyehouses and Bleacheries. Joseph Woodman. *Textile Colorist*, Vol. 44 (1922), No. 520, pp. 245–47.

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

Accidents at Metallurgical Works in the United States during the Calendar Year 1920. W. W. Adams. *Technical Paper* 297. 28 pp. Paper, 5 cents.

Analysis of Detonating and Priming Mixtures. C. A. Taylor and W. H. Rinkenbach. *Technical Paper* 282. 33 pp. Paper, 5 cents.

Analytical Distillations of Typical Shale Oils. M. J. Gavin. *Reports of Investigations* 2332. 12 pp. Issued March 1922.

Bibliography of Literature on Sampling. Compiled by W. J. Sharwood and M. W. von Bernewitz. *Reports of Investigations* 2336. 1 p. Issued March 1922.

Drilling and Dustiness of Metal-Mine Air. D. Harrington. *Reports of Investigations* 2339. 6 pp. Issued March 1922.

Epsomite. R. B. Ladoo. *Reports of Investigations* 2333. 5 pp. Issued March 1922.

Fighting a Mine Fire with Its Own Gases. C. A. Allen and A. C. Watts. *Reports of Investigations* 2325. 8 pp. Issued February 1922.

Metal-Mine Accidents in the United States during the Calendar Year 1920. W. W. Adams. *Technical Paper* 299. 99 pp. Paper, 10 cents. 1922.

Performance of Fan-Pipe Installations in Metal Mines. D. Harrington. *Reports of Investigations* 2320. 4 pp. Issued February 1922.

Physiological Effects of Exposure to Low Concentrations of Carbon Monoxide. R. R. Sayers, F. V. Meriwether and W. P. Yant. *Reports of Investigations* 2338. 6 pp. Issued March 1922.

Procedure for Establishing a List of Permissible Carbon Monoxide Indicators. Fees, Character of Tests, and Conditions under Which Indicators Will Be Tested. *Schedule* 18. 7 pp.

Production of Gasoline by Cracking Heavier Oils. E. W. Dean and W. A. Jacobs. *Technical Paper* 258. Paper, 5 cents.

Quarry Accidents in the United States during the Calendar Year 1920. *Technical Paper* 295. 66 pp. Paper 10 cents. 1922.

Recent Articles on Petroleum and Allied Substances. Compiled by E. H. Burroughs. *Reports of Investigations* 2330. 53 pp. Issued February 1922.

Specifications for Petroleum Products Adopted by the Interdepartmental Petroleum Specifications Committee, Effective January 23, 1922. Amended March 1, 1922. These specifications have been officially adopted by the Federal Specifications Board for the use of the various departments and independent establishments of the Government. *Technical Paper* 305. 40 pp. Paper, 5 cents.

Summarized Reports of Principal Investigations Being Conducted by the Bureau of Mines for Fiscal Year beginning July 1, 1921. 186 pp.

Test of Hand Extinguishers on Zinc-Dust Fires. S. H. Katz and J. J. Bloomfield. *Reports of Investigations* 2335. 6 pp. Issued March 1922.

The Northwest Experiment Station of the Federal Bureau of Mines. C. E. Williams. *Reports of Investigations* 2337. 4 pp. Issued March 1922.

The Smoke Problem. O. P. Hood. *Reports of Investigations* 2323. 5 pp. Issued February 1922.

The Use of Electrolytes in the Purification and Preparation of Clays. H. G. Schurecht. *Technical Paper* 281. 47 pp. Paper, 10 cents.

Use of Low-Pressure Gas Burners in Oil-Feed Boilers. M. P. Youker. *Reports of Investigations* 2329. 8 pp. Issued February 1922.

Bureau of Standards

Weighing by Substitution. C. A. Briggs and E. D. Gordon. *Technologic Paper* 208. Paper, 5 cents.

Congress

Tariff: An Act to Provide revenue, to regulate commerce with foreign countries, to encourage the industries of the United States, and for other purposes. H. R 7456. Report 595. Reported by Mr. McCumber with amendments April 10, 1922 (Calendar Day, April 11). 438 pp.

Congressional Committees

Decimal System. American decimal system of weights and measures, by Samuel Russell. Statement, December 20, 1921. 20 pp 1922.

Hearings before the Committee on Finance, United States Senate, on the Proposed Tariff Act of 1921 (H. R. 7456). Free List. Revised and Indexed. 693 pp.

Metric System. Ladd Metric Bill, Its Fallacy and Futility. Statement of Samuel Russell, December 16, 1921. 8 pp. 1922.

Metric System. Statement by Samuel S. Dale at hearings before subcommittee on S. 2267, to fix metric system of weights and measures for certain uses, December 14, 1921. 24 pp. 1922.

Muscle Shoals Propositions. Hearings before the Committee on Military Affairs, House of Representatives.

Part 11—Statements of F. D. Mahoney (Alabama Power Co.), Hon. S. Hubert Dent, Jr., Thomas W. Martin (President, Alabama Power Co.), Hon. William B. Oliver, M. C., Alabama, Major John G. Booton, Ordnance Department, U. S. A. February 27–March 2, 1922. 195 pp.

Part 12—Statements of Frederick E. Engstrum, Hon. Marion Butler, Thomas W. Martin, Francis E. Frothingham J. H. Levering, William B. Mayo, Gray Silver, Hon. William B. Oliver, Hon. Ed. B. Almon, Hon. William B. Bankhead, Hon. Joseph W. Byrns, Hon John McDuffie, Col. J. W. Joyes and Dr. Charles L. Parsons. March 3, 6, 7, 8, 10, and 13, 1922. 240 pp.

Department of Commerce

Artificial Dyestuffs Imported into the United States 1913–14. Supplemental Statistics to Accompany Agents Series 121. 47 pp.

General Supply Committee

Specifications and Proposals for Supplies, Fiscal Year 1923. Class 4. Drugs and Medicines, and Chemicals. 34 pp.

Geological Survey

Cement in 1920. E. F. Burchard. Separate from Mineral Resources of the United States, 1920, Part II. 20 pp. Published March 7, 1922.

Field Examination of Water. W. D. Collins. 13 pp.

Quicksilver in 1920. F. L. Ransome. With a Supplementary Bibliography. I. P. Evans. Separate from Mineral Resources of the United States, 1920, Part I. 21 pp. Published March 27, 1922.

Stone in 1920. G. F. Loughlin and A. T. Coons. Separate from Mineral Resources of the United States, 1920, Part II. 38 pp. Published March 6, 1922.

Labor Statistics Bureau

Carbon Monoxide Poisoning. Alice Hamilton *Bulletin* 291. Industrial Accidents and Hygiene Series. 47 pp. Paper, 10 cents.

Public Health Service

City Health Officers, 1921, Directory of Those in Cities of 10,000 or More Population. *Reprint* 702 from Public Health Reports. 12 pp. Paper, 5 cents.

Improved Method for the Preparation of Vitamin-Activated Fuller's Earth. Atherton Seidell. *Public Health Reports* 37 (April 7, 1922), 801–3.

Keeping Qualities of Market Samples of Neoarsphenamine While in Ampule. G. B. Roth. *Reprint* 700 from Public Health Reports. 19 pp. Paper, 5 cents.

State and Insular Health Authorities, 1921: Directory, with Data as to Appropriations and Publications. *Reprint* 706 from Public Health Reports. 20 pp. Paper, 5 cents.

The Loading of Filter Plants. H. W. Streeter. *Public Health Reports* 37 (March 31, 1922), 741–53.

United States Public Health Service, Information for Persons Desiring to Enter Regular Corps of Service. R. C. Williams. *Reprint* 719 from Public Health Reports. 6 pp.

Tariff Commission

Tariff Information Surveys. Revised edition, 1922. FL-24. On articles in Paragraphs 536–544 of Tariff Act of 1913 and related articles in other paragraphs. Cryolite, graphite, and magnesite. 65 pp. Paper, 5 cents.

MARKET REPORT—APRIL, 1922

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

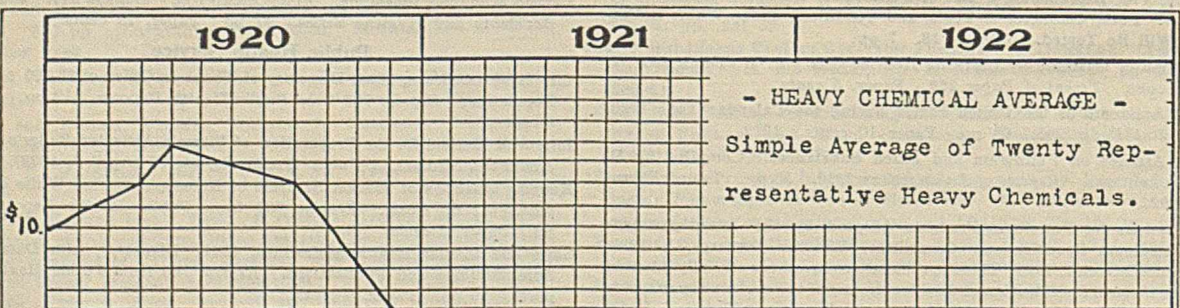
INORGANIC CHEMICALS

		Apr. 1	Apr. 15
Acid, Boric, cryst., bbls.	lb.	.12$^3/_4$	.12$^3/_4$
Hydrochloric, com'l, 20°	lb.	.01$^1/_4$	.01$^1/_4$
Hydrofluoric, 30 p. c., bbls.	lb.	.07	.07
Hydriodic, sp. gr. 1.150	oz.	.19	.19
Nitric, 42°	lb.	.06$^3/_4$	.06$^3/_4$
Phosphoric, 50% tech	lb.	.09	.09
Sulfuric, C. P.	lb.	.07	.07
Chamber, 66° tks. wks.	ton	16.00	16.00
Oleum 20%	ton	22.00	22.00
Alum, Ammonia, lump	lb.	.03$^1/_2$	.03$^1/_2$
Potash, lump	lb.	*.03$^1/_4$	*.03$^1/_4$
Chrome	lb.	.06$^1/_2$	.06$^1/_2$
Soda, ground	lb.	.03$^1/_2$	.03$^1/_2$
Aluminium Sulfate (iron-free)	lb.	.02$^1/_2$	.02$^1/_2$
Ammonium Carbonate, pwd	lb.	*.07	*.07
Ammonium Chloride, gran	lb.	.07$^1/_2$	.07$^1/_2$
Ammonia, Anhydrous	lb.	.30	.30
Ammonia Water, drums, 26°	lb.	.07$^1/_2$	.07$^1/_2$
Arsenic, white	lb.	.07	.06$^3/_4$
Barium Chloride	ton	*80.00	*100.00
Nitrate	lb.	*.06	*.06
Barytes, white	ton	28.00	28.00
Bleaching Powd., 35%, works,	100 lbs.	1.75	1.75
Borax, cryst., bbls.	lb.	.05$^1/_2$	.05$^1/_2$
Bromine, pure, wks	lb.	.23	.23
Calcium Chloride, fused, f. o. b. N. Y.	ton	24.50	24.50
Chalk, precipitated, light	lb.	.04	.04
China Clay, imported	ton	18.00	18.00
Chlorine, liquid	lb.	.06	.06
Copper Sulfate	100 lbs.	5.40	5.40
Feldspar	ton	8.00	8.00
Fuller's Earth	100 lbs.	1.00	1.00
Iodine, resublimed	lb.	4.05	4.05
Lead Acetate, white crystals	lb.	.11	.11
Nitrate	lb.	.15	.15
Red American	lb.	.08	.08
White American	lb.	.07$^1/_4$	.07$^1/_4$
Lime Acetate	100 lbs.	1.75	1.75
Lithium Carbonate	lb.	1.40	1.40
Magnesium Carbonate, tech.	lb.	.06	.06
Magnesite	ton	72.00	50.00
Mercury flask	75 lbs.	49.00	50.00
Phosphorus, yellow	lb.	*.25	*.25
Red	lb.	*.25	*.25
Plaster of Paris	bbl.	4.25	4.25
Potassium Bichromate	lb.	.10	.10
Bromide, imported	lb.	*.17	*.16
Carbonate, calc., 80–85%	lb.	.04$^1/_2$	.04$^1/_2$
Chlorate, cryst.	lb.	*.06	*.06
Hydroxide, 88–92%	lb.	*.06	*.06
Iodide, bulk	lb.	3.15	3.15
Potassium (*Concluded*)			
Nitrate	lb.	.08	.08
Permanganate U. S. P.	lb.	*.14	*.14
Prussiate, Red	lb.	*.65	*.65
Yellow	lb.	.26$^1/_2$	.27$^1/_2$
Salt Cake, bulk	ton	17.00	17.00
Silver Nitrate	oz.	.43$^3/_4$	.44
Soapstone, in bags	ton	12.00	12.00
Soda Ash, 58%, bags	100 lbs.	*1.80	*1.80
Caustic, 76%	100 lbs.	*3.60	*3.60
Sodium Acetate	lb.	.04	.04
Bicarbonate	100 lbs.	2.00	2.00
Bichromate	lb.	.07$^1/_2$	.07$^1/_4$
Bisulfite, powd	lb.	.04$^1/_2$	.04$^1/_2$
Chlorate	lb.	.07	.07
Cyanide, 96–98%	lb.	.26	.25
Fluoride, technical	lb.	.10	.10
Hyposulfite, bbls.	100 lbs.	3.25	3.25
Nitrate, 95%	100 lbs.	2.85	2.85
Nitrite	lb.	.09$^1/_2$	.09$^1/_2$
Prussiate, yellow	lb.	.16$^3/_4$	.16
Phosphate (di-sodium), tech.	lb.	.04	.04
Silicate, 40°	lb.	.01	.01
Sulfide, 60% fused	lb.	*.04$^1/_4$	*.04$^1/_4$
Strontium Nitrate	lb.	*.07$^1/_2$	*.07$^1/_2$
Sulfur, flowers	100 lbs.	3.00	3.00
Crude, mines	long ton	14.00	14.00
Talc, American, white	ton	17.00	17.00
Tin Bichloride, 50% sol'n	lb.	.10$^1/_4$	.10$^1/_4$
Oxide	lb.	.37	.37
Zinc Chloride, U. S. P.	lb.	.35	.35
Oxide, bbls.	lb.	.08	.08

*Resale or Imported (not an American makers' price).

ORGANIC CHEMICALS

		Apr. 1	Apr. 15
Acetanilide, U. S. P. bbls.	lb.	.31	.31
Acid, Acetic, 28 p. c.	100 lbs.	2.37$^1/_2$	2.37$^1/_2$
Glacial	lb.	.08$^1/_2$	.08$^1/_2$
Acetylsalicylic, 100 lbs.	lb.	.80	.80
Benzoic, U. S. P., ex-toluene	lb.	.58	.55
Carbolic, cryst., U. S. P., drs.	lb.	.14	.14
50- to 110-lb. tins	lb.	.21	.21
Citric, crystals, kegs	lb.	*.45	*.45$^1/_2$
Oxalic, cryst., bbls., wks.	lb.	.11$^1/_2$	.11$^1/_2$
Pyrogallic, resublimed	lb.	1.60	1.60
Salicylic, bulk, U. S. P.	lb.	.26	.26
Tannic, U. S. P., bbls.	lb.	.65	.65
Tartaric, crystals, U. S. P.	lb.	*.26	*.26$^1/_2$
Trichloroacetic, U. S. P.	lb.	4.40	4.40
Acetone, drums	lb.	.09	.09
Alcohol, denatured, complete	gal.	.30	.30
Ethyl, 190 proof, bbls.	gal.	4.75	4.75
Amyl Acetate	gal.	2.00	2.00



Courtesy of Drug & Chemical Markets

		Apr. 1	Apr. 15
Caffeine Alkaloid,	lb.	3.75	3.75
Camphor, Jap, refined, cases	lb.	.86	.82
Carbon Bisulfide, c/l	lb.	.06	.06
Tetrachloride	lb.	.10	.10
Chloroform, U. S. P., drums	lb.	.37	.37
Creosote, U. S. P	lb.	.40	.40
Cresol, U. S. P	lb.	.12	.13
Dextrin, corn	100 lbs.	2.99	2.99
Imported Potato	lb.	.08$^{1}/_{2}$	.09
Ether, U. S. P., conc., 100 lbs.	lb.	.14	.14
Formaldehyde, bbls	lb.	.08$^{1}/_{2}$	.08$^{1}/_{2}$
Glycerol, dynamite, drums	lb.	.13$^{1}/_{2}$	.13
Methanol, pure, bbls	gal.	.75	.72
Methylene Blue, Med	lb.	3.50	3.50
Petrolatum, snow-white	lb.	.12$^{1}/_{2}$	.12$^{1}/_{2}$
Light Amber	lb.	.04$^{1}/_{2}$	.04$^{1}/_{2}$
Green	lb.	.02$^{3}/_{4}$	.02$^{3}/_{4}$
Pyridine	gal.	1.75	1.75
Starch, corn, Pow'd	100lbs.	2.32	2.32
Potato, Jap	lb.	.07	.07
Rice	lb.	.18	.18
Sago	lb.	.04	.04

OILS, WAXES, ETC.

		Apr. 1	Apr. 15
Beeswax, pure, white	lb.	.35	.35
Black Mineral Oil, 29 gravity	gal.	.22	.22
Castor Oil, No. 3	lb.	.10$^{1}/_{2}$	.10$^{1}/_{2}$
Ceresin, yellow.	lb.	.08	.08
Corn Oil, crude, tanks, mills	lb.	.10	.10
Cottonseed Oil, crude, f. o. b. mill.	lb.	.10	.10
Linseed Oil, raw (car lots)	gal.	.79	.83
Menhaden Oil, crude (southern)	gal.	.40	.40
Neat's-foot Oil, 20°	lb.	.24	.24
Paraffin, 128–130 m. p., ref	lb.	.04	.04
Paraffin Oil, high viscosity	gal.	.45	.45
Rosin, "F" Grade, 280 lbs.	bbl.	5.35	5.30
Rosin Oil, first run	gal.	.36	.36
Shellac, T. N.	lb.	.78	.82
Spermaceti, cake	lb.	.30	.30
Sperm Oil, bleached winter, 38°	gal.	1.69	1 69
Stearic Acid, double-pressed	lb.	.10	.09$^{1}/_{2}$
Tallow Oil, acidless	lb.	.10$^{1}/_{4}$	.10$^{1}/_{4}$
Tar Oil, distilled	gal,	.60	.60
Turpentine, spirits of	gal.	.85	.86

METALS

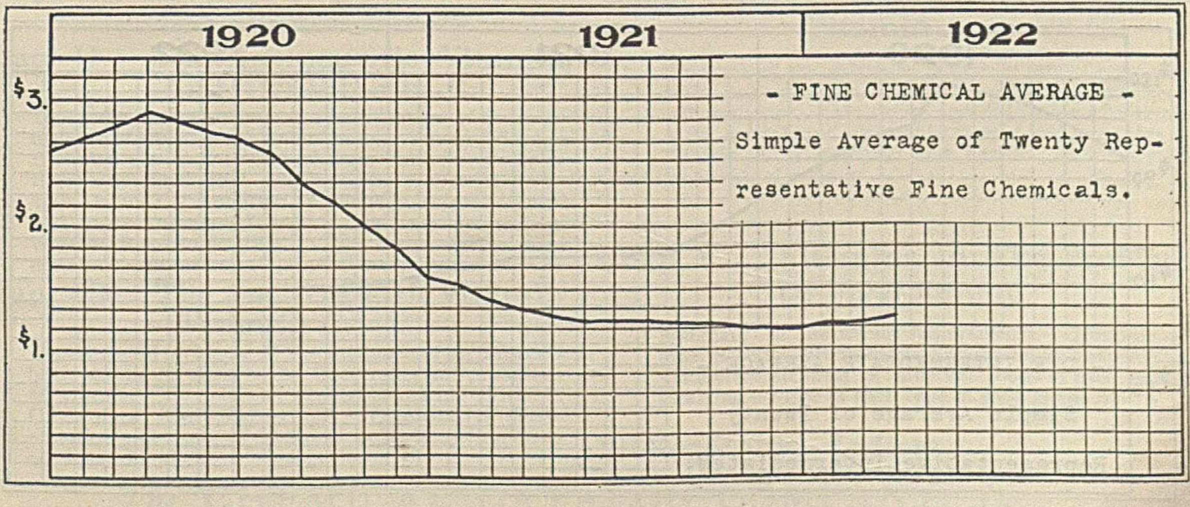
		Apr. 1	Apr. 15
Aluminium, No. 1, ingots	lb.	.17	.17
Antimony, ordinary	100 lbs.	4.35	4.50
Bismuth	lb.	2.10	2.00
Copper, electrolytic	lb.	.12$^{3}/_{4}$	.12$^{3}/_{4}$
Lake	lb.	.12$^{3}/_{4}$	.12$^{7}/_{8}$
Lead, N. Y.	lb.	.05	.05
Nickel, electrolytic	lb.	.41	.41
Platinum, refined, soft	oz.	90.00	90.00
Quicksilver, flask	75 lbs. ea.	49.00	50.00
Silver, foreign	oz.	.64$^{7}/_{8}$	.65$^{1}/_{2}$
Tin	lb.	.29$^{1}/_{4}$	.31
Tungsten Wolframite	per unit	2.00	2·00
Zinc, N. Y.	100 lbs.	5.00	5.10

FERTILIZER MATERIALS

		Apr. 1	Apr. 15
Ammonium Sulfate, export	100 lbs.	3.65	3.65
Blood, dried, f. o. b. N. Y.	unit	4.00	4.00
Bone, 3 and 50, ground, raw	ton	30.00	30.00
Calcium Cyanamide, unit of Ammonia		2.25	2.25
Fish Scrap, domestic, dried, f. o. b. works	unit	3.25 & .10	3.25 & .10
Phosphate Rock, f. o. b. mine:			
Florida Pebble, 68%	ton	5.00	5.00
Tennessee, 78–80%	ton	8.00	8.00
Potassium Muriate, 80%	unit	.60	.60
Pyrites, furnace size, imported	unit	.14	.14
Tankage, high-grade, f. o. b. Chicago	unit	3.25 & .10	3.50 & .10

COAL-TAR CHEMICALS

		Apr. 1	Apr. 15
Crudes			
Anthracene, 80–85%	lb.	.75	.75
Benzene, pure, tanks	gal.	.29	.29
Cresol, U. S. P.	lb.	.12	.12
Cresylic Acid, 97–99%	gal.	.50	.50
Naphthalene, flake	lb.	.07	.07
Phenol, drums	lb.	.12	.12
Toluene, pure, tanks	gal.	.30	.30
Xylene, 2 deg. dist. range, tanks	gal.	.45	.45
Intermediates			
Acids:			
Anthranilic	lb.	1.10	1.10
Benzoic tech	lb.	.50	.50
Broenner's	lb.	1.55	1.55
Cleve's	lb.	1.50	1.50
Gamma	lb.	1.90	1.90
H	lb.	.85	.85
Metanilic	lb.	1.00	1.00
Monosulfonic F	lb.	2.30	2.30
Naphthionic, crude	lb.	.65	.65
Nevile & Winther's	lb.	1.25	1.25
Phthalic	lb.	.32	.32
Picric	lb.	.20	.20
Sulfanilic	lb.	.22	.22
Tobias'	lb.	1.50	1.50
Aminoazobenzene	lb.	1.15	1.15
Aniline Oil	lb.	.15$^{1}/_{2}$	.15$^{1}/_{2}$
Aniline Salt	lb	.24	.22
Anthraquinone	lb.	1.40	1.40
Bayer's Salt	lb.	1.00	1.00
Benzaldehyde, tech	lb.	.55	.55
U. S. P.	lb.	1.40	1.40
Benzidine (base)	lb.	.85	.85
Benzidine Sulfate	lb.	.70	.70
Diaminophenol	lb.	5.50	5.50
Dianisidine	lb.	4.75	4.75



- FINE CHEMICAL AVERAGE -

Simple Average of Twenty Representative Fine Chemicals.

Courtesy of Drug & Chemical Markets

		Apr. 1	Apr. 15
p-Dichlorobenzene	lb.	.17	.17
Diethylaniline	lb.	.60	.60
Dimethylaniline	lb.	.36	.36
Dinitrobenzene	lb.	.20	.20
Dinitrotoluene	lb.	.25	.25
Diphenylamine	lb.	.60	.60
G Salt	lb.	.65	.65
Hydroquinol	lb.	1.35	1.35
Metol (Rhodol)	lb	3.50	3.50
Monochlorobenzene	lb.	.10	.10
Monoethylaniline	lb.	1.00	1.00
α-Naphthylamine	lb.	.30	.30
β-Naphthylamine (Sublimed)	lb.	1.50	1.50
β-Naphthol, dist	lb.	.28	.28
m-Nitroaniline	lb.	.77	.77
p-Nitroaniline	lb.	.77	.77
Nitrobenzene, crude	lb.	.09	.09
Rectified (Oil Mirbane)	lb.	.10	.10
p-Nitrophenol	lb.	.75	.75
p-Nitrosodimethylaniline	lb.	—	—
o-Nitrotoluene	lb.	.15	.15
p-Nitrotoluene	lb.	.70	.70
m-Phenylenediamine	lb	1.05	1.05
p-Phenylenediamine	lb.	1.50	1.50
Phthalic Anhydride	lb.	.35	.35
Primuline (Base)	lb.	2.00	2.00
R Salt	lb.	.60	.60
Resorcinol, tech	lb.	1.50	1.50
U. S. P	lb	1.75	1.75
Schaeffer Salt	lb.	.70	.70
Sodium Naphthionate	lb	.70	.70
Thiocarbanilide	lb.	.37	.37
Tolidine (Base)	lb.	1.20	1.20
Toluidine, mixed	lb	.30	.30
o-Toluidine	lb.	.20	.20
p-Toluidine	lb.	1.00	1.00
m-Toluylenediamine	lb	1.05	1.05
Xylidine, crude	lb.	.45	.45

COAL-TAR COLORS

Acid Colors

		Apr. 1	Apr. 15
Black	lb.	.80	.80
Blue	lb.	1.50	1.50
Fuchsin	lb.	2.00	2.00
Orange III	lb.	.50	.50
Red	lb.	.85	.85
Alkali Blue, domestic	lb.	4.50	4.50
Azo Carmine	lb.	4.00	4.00
Azo Yellow	lb.	1.50	1.50
Erythrosin	lb.	6.00	6.00
Indigotin, conc	lb.	2.50	2.50
Paste	lb.	1.50	1.50
Naphthol Green	lb.	1.60	1.60
Ponceau	lb.	.80	.80
Scarlet 2R	lb.	.70	.70

Direct Colors

		Apr. 1	Apr. 15
Black	lb.	.55	.55
Blue 2B	lb.	.60	.60
Brown R	lb.	.85	.85
Fast Red	lb.	2.35	2.35
Yellow	lb.	2.00	2.00
Violet, conc	lb.	1.10	1.10
Chrysophenine, domestic	lb.	1.10	1.10
Congo Red, 4B Type	lb.	.90	.90
Primuline, domestic	lb.	1.75	1.75

Oil Colors

		Apr. 1	Apr. 15
Black	lb.	.70	.70
Blue	lb.	1.25	1.25
Orange	lb	.95	.95
Red III	lb.	1.65	1.65
Scarlet	lb.	1.00	1.00
Yellow	lb.	1.25	1.25
Nigrosine Oil, soluble	lb.	.90	.90

Sulfur Colors

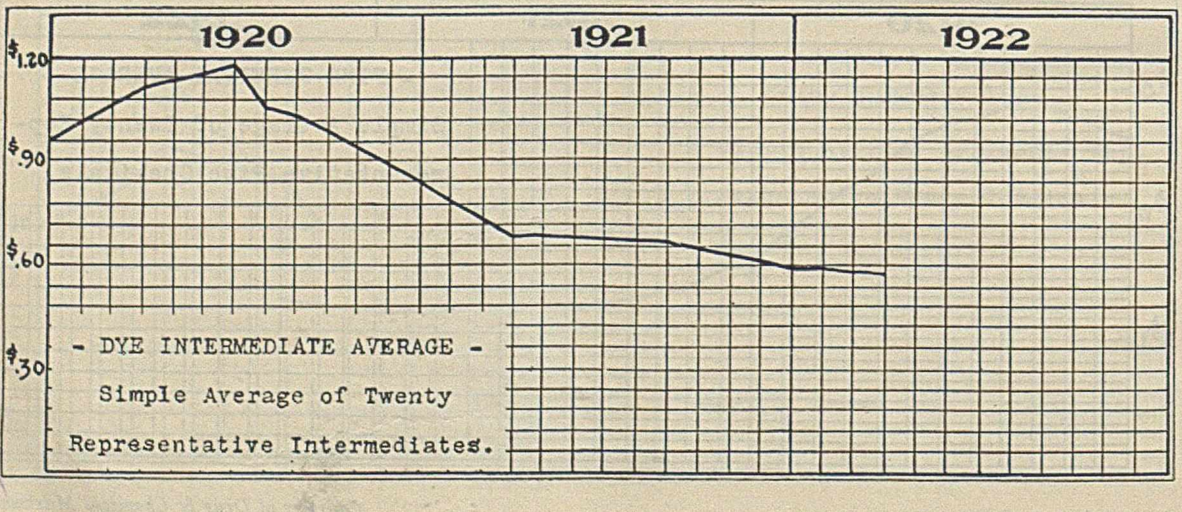
		Apr. 1	Apr. 15
Black	lb.	.20	.20
Blue, domestic	lb.	.60	.60
Brown	lb.	.35	.35
Green	lb.	1.00	1.00
Yellow	lb.	.75	.75

Chrome Colors

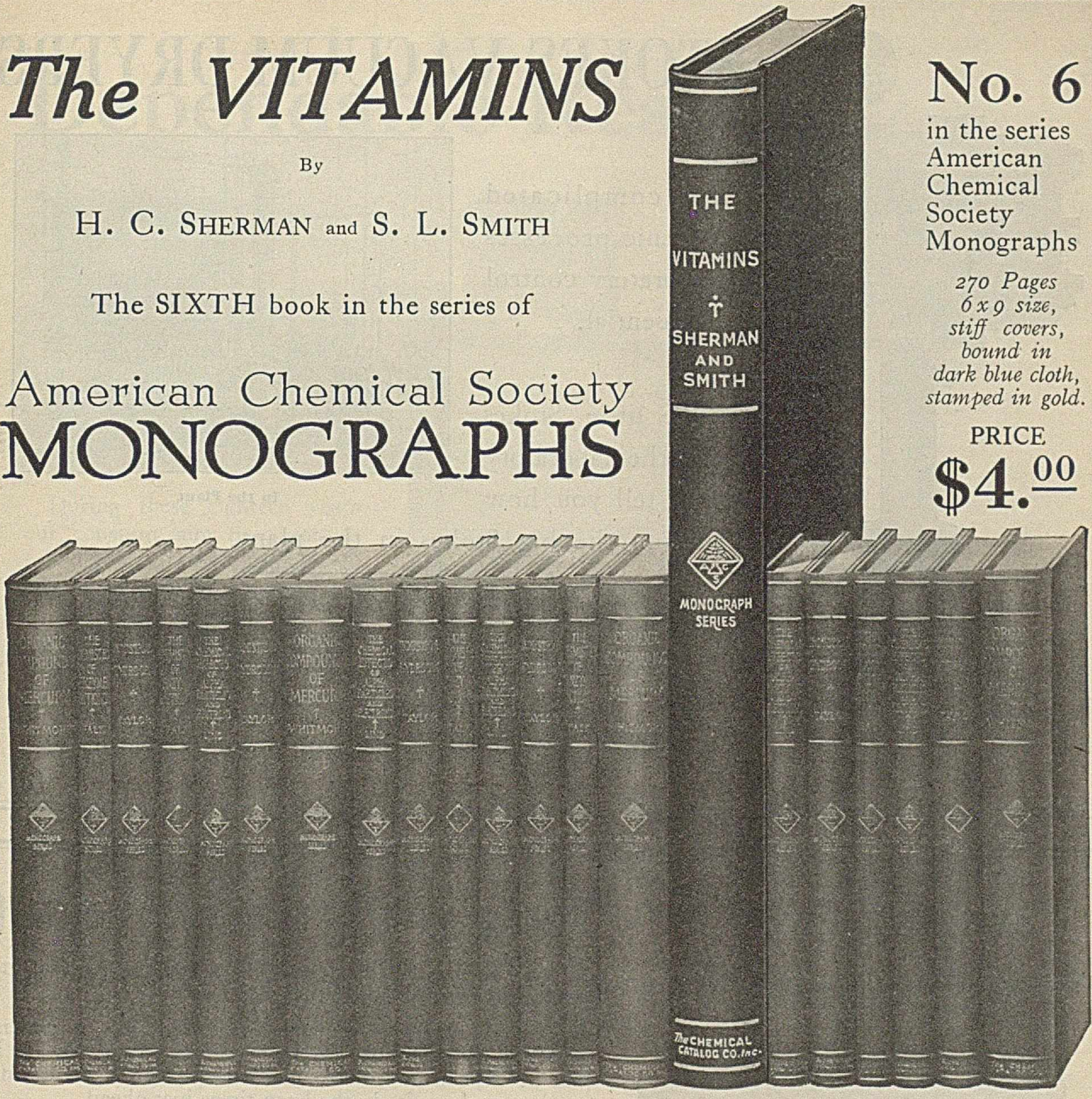
		Apr. 1	Apr. 15
Alizarin Blue, bright	lb.	5.00	5.00
Alizarin Red, 20% paste	lb.	.60	.60
Alizarin Yellow G	lb.	.85	.85
Chrome Black, domestic	lb.	.55	.55
Chrome Blue	lb.	.75	.75
Chrome Green, domestic	lb.	1.50	1.50
Chrome Red	lb.	1.75	1.75
Gallocyanin	lb.	2.30	2.30

Basic Colors

		Apr. 1	Apr. 15
Auramine, O, domestic	lb.	1.50	1.50
Auramine, OO	lb.	2.50	2.50
Bismarck Brown R	lb.	.70	.70
Bismarck Brown G	lb.	1.00	1.00
Chrysoidine R	lb.	.75	.75
Chrysoidine Y	lb.	.75	.75
Green Crystals, Brilliant	lb.	2.25	2.25
Indigo, 20% paste	lb.	.45	.45
Fuchsin Crystals, domestic	lb.	3.00	3.00
Magenta Acid, domestic	lb.	2.00	2.00
Malachite Green, crystals	lb.	1.60	1.60
Methylene Blue, tech	lb.	1.50	1.50
Methyl Violet 3 B	lb.	1.75	1.75
Nigrosine, spts. sol	lb.	.70	.70
Water sol., blue	lb.	.60	.60
Jet	lb.	.90	.90
Phosphine G., domestic	lb.	2.50	2.50
Rhodamine B, extra conc	lb.	8.00	8.00
Victoria Blue, base, domestic	lb.	3.50	3.50
Victoria Green	lb.	1.50	1.50
Victoria Red	lb.	7.00	7.00
Victoria Yellow	lb.	7.00	7.00



Courtesy of Drug & Chemical Markets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SMITH
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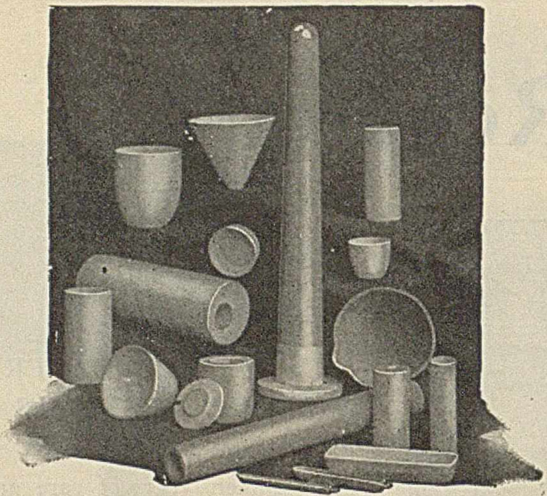
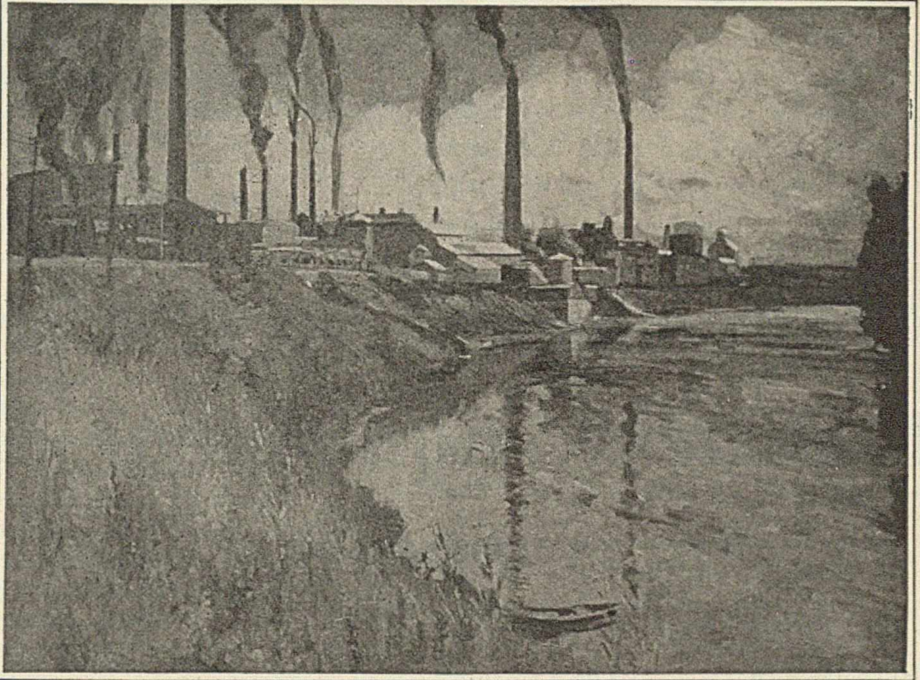


TRADE DOW MARK



PARTIAL VIEW OF THE DOW CHEMICAL CO. PLANT

How Do You Choose Chemicals For Industrial or Pharmaceutical Purposes?

Few realize how varied are the industries and how wide the array of products and processes now using and depending on regular supplies of DOW Chemicals. Many a nationally known remedy, many a solvent and innumerable other products of national repute are either based upon a DOW Chemical as a finished product or are the results of the use of some of the eighty odd chemicals which bear the DOW Trade Mark.

DOW solvents are used in hundreds of manufacturing processes; DOW Dyes have been a boon to many a textile manufacturer. The photo-engraver would no more think of doing without etching solutions from DOW than the orchardist would fail in protecting his fruit with DOW Insecticides or the tanner get along without the particular DOW Chemicals he uses.

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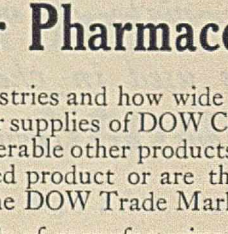

Eastman Organic Chemicals

MADE IN U. S. A.

Note Quality Specifications

492	*	Dimethyl-p-phenylenediamine Hydrochloride *see* p-Aminodimethylaniline Hydrochloride
729	*	2.4-Dimethylquinoline BP 145-147°/10 mm.
724	*	2.6-Dimethylquinoline MP 58°
772	*	2.4-Dimethylquinoline Sulfate
P 328		Dimethyl Sulfate *see* Methyl Sulfate
646	*	Dimethyl p-Toluidine BP 97-100°/10 mm.
1019	*	Dimethyl-o-toluidine BP 69-70°/10 mm.
1180	*	Di-α-naphthylurea MP 269-270°
395	*	2.4-Dinitro-6-aminophenol *see* Picramic Acid
99	*	m-Dinitrobenzene MP 89-89.5°
T 99		m-Dinitrobenzene (Techn.) MP 80-83°
671	*	2.4-Dinitrobenzoic Acid MP 178-179°
635	*	3.5-Dinitrobenzoic Acid MP 203-205°
100	*	m-Dinitrobenzoyleneurea MP 268-269°
101	*	2.4-Dinitrochlorobenzene MP 50-52°
P 101		2.4-Dinitrochlorobenzene (Pract.) MP 47-48°
782	*	Dinitrohydroquinone Diacetate MP 94-95°
987	*	1.5-Dinitronaphthalene MP 209.5-211.5°
T 1001		Dinitronaphthalene (Techn.)
102	*	2.4-Dinitrophenol MP 112-113°

Specifications of Quality

Our own laboratory observations of melting points and boiling ranges and other purity criteria are given, wherever possible, after each chemical named in our new list. Our chemicals will not fall below these specifications of quality.

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1300 fine organic chemicals are available for laboratory, research, and university uses.

Prices

In many instances selling prices of our chemicals have been reduced. These reductions are shown in our new list.

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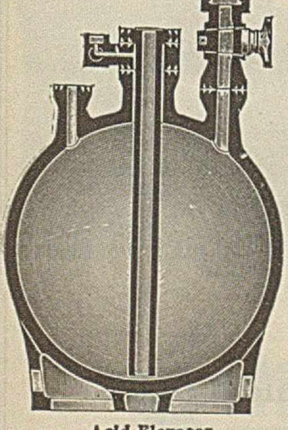

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made in eleven sizes
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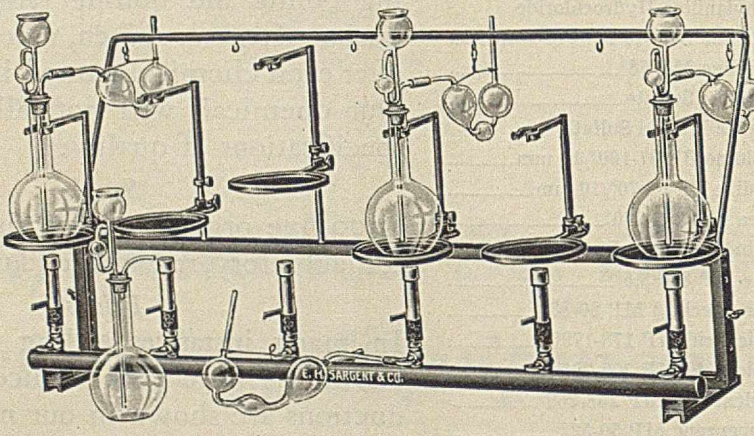
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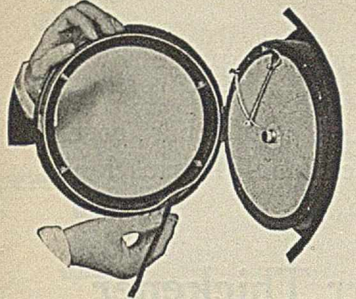

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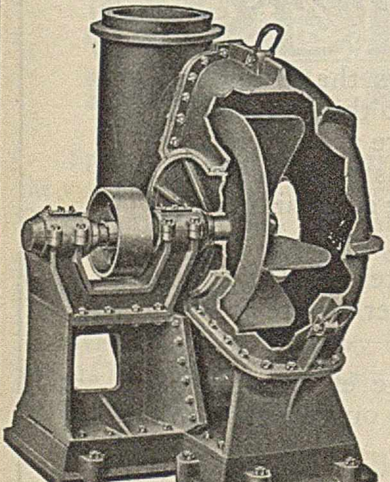

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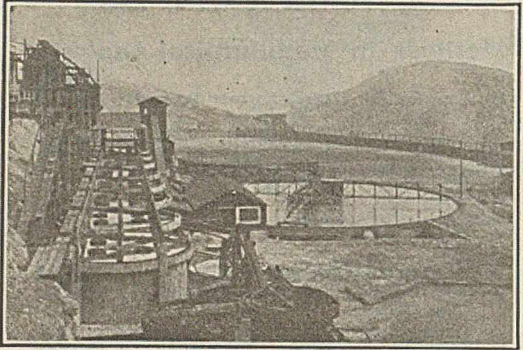

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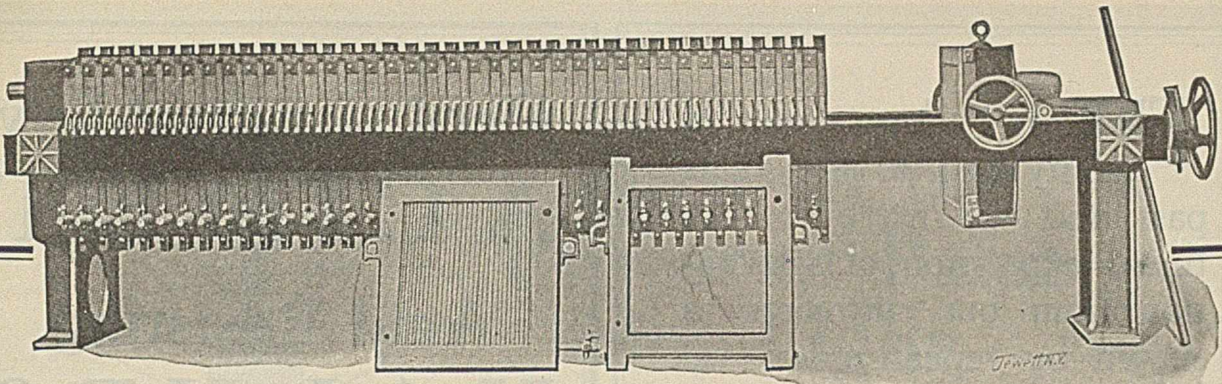

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Sperry engineers do not say that a stock press will do the work—at least not until they are fully satisfied it will. Each filtering problem referred to Sperry is carefully studied, tests made and data compiled before the final design of the press is made.

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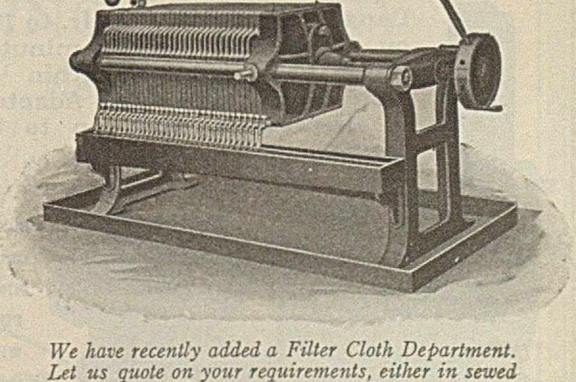

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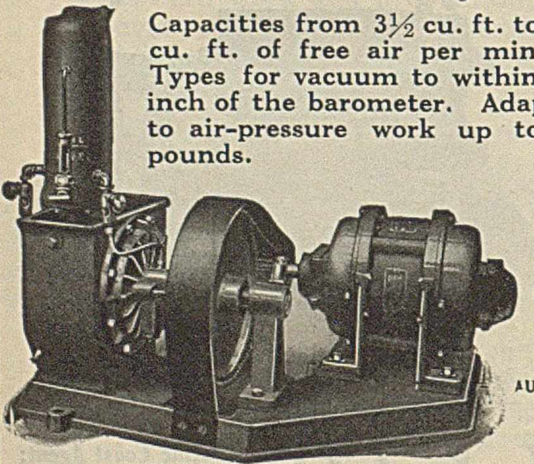

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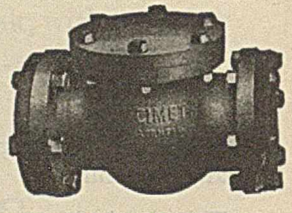
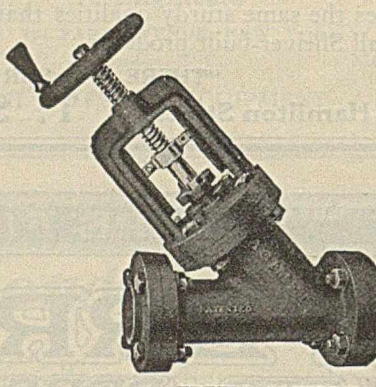
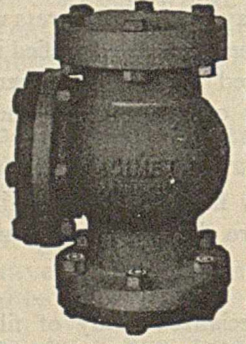
The only valves that will absolutely withstand the influence of sulphuric acid of any degree and other corrosive liquids in their various forms.



HORIZONTAL CHECK



FREFLO PATTERN



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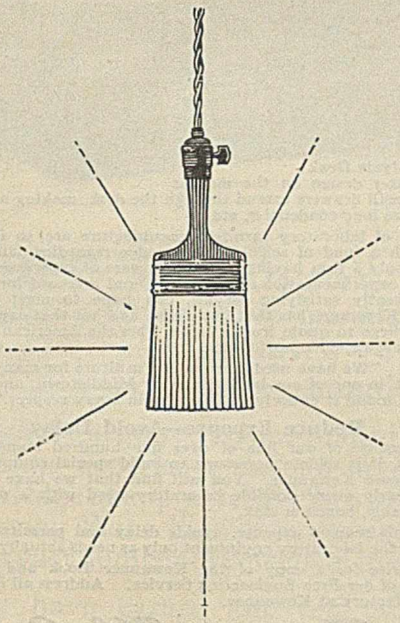

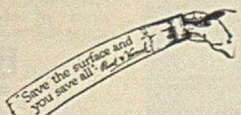
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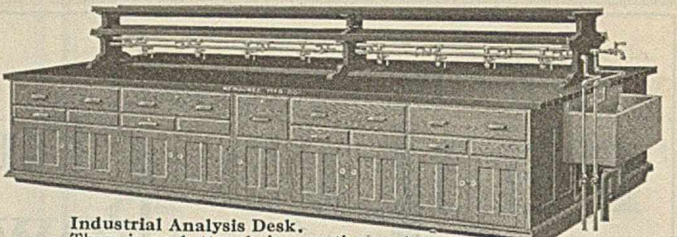
meets the exacting requirements of America's largest industrial plants. The correct design, superior materials and skilled workmanship which go into every piece of Kewaunee Equipment are making this furniture standard in the Industrial Laboratory field.

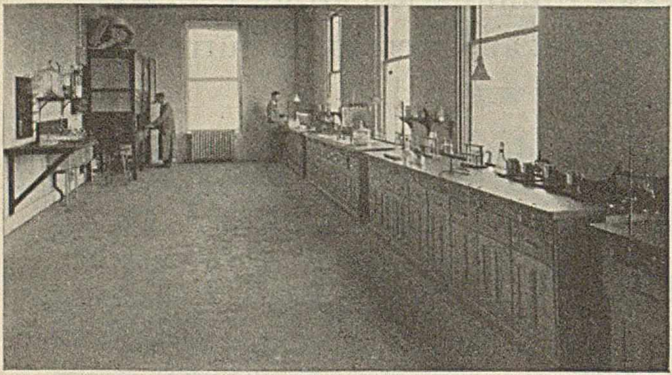


Industrial Analysis Desk. There is no better design on the market today. The small drawers extend through the desk, making an excellent place to store long condensers, etc.

The details of laboratory furniture manufacture are so intricate and require such a fund of scientific knowledge regarding laboratory operation that only a firm having back of it years of experience, years of conscientious experimentation and progress, and a record for having rendered consistently satisfying service, can hope to meet modern requirements. Kewaunee has that knowledge and has that experience.

It is a privilege to quote from a letter from the American Rolling Mill Co., Middletown, Ohio, as follows:

> "We have used Kewaunee Furniture for many years in one of our laboratories at Middletown, and have found it entirely satisfactory in every respect."



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HORNE'S Dry Lead may be added directly to sugar solutions to precipitate coloring matter and other impurities without affecting the volume of the solution or the concentration of the sugar. In sugar analysis this possesses great advantages over any other method because of its scientific accuracy and efficiency in saving time.

For polarizing raw sugars and other products the normal weight of the sample is dissolved in a graduated flask and the solution made up exactly to 100cc. The dry lead powder is then sprinkled in gradually, with mixing, until sufficient decolorization and flocculation have been affected. The clarified solution is filtered and polarized. The precipitate formed in this way is outside of the 100cc and therefore does not modify the concentration of the sucrose solution. This will ensure correct polarization.

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THIS SHORT METHOD OF USING HORNE'S DRY LEAD INSTEAD OF A SOLUTION OF LEAD SUBACETATE, ENABLES FIVE TESTS TO BE MADE IN THE TIME USUALLY REQUIRED TO MAKE THREE TESTS.

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Since 1883, the makers of "Proctor" Dryers have manufactured drying machinery exclusively—a longer time than any other organization.

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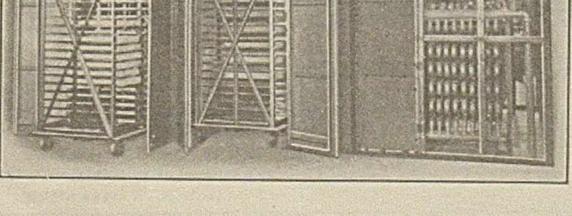
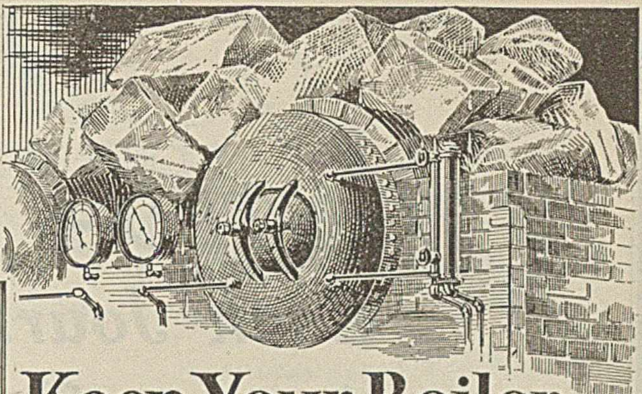


"Proctor" Dryer (Truck type), the most widely used machine for drying Paint Colors, Dye Stuffs, Chemicals and many similar materials. Other types of "Proctor" Dryers include Cabinet-Tray, Tunnel-Truck, Automatic-Tray and Rotary Dryers.



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By packing ice around your boiler you will reduce the temperature. This makes it more difficult to keep steam up. More coal will be required. Your fuel bills will be higher.

Ridiculous? Of course it is! But not any more ridiculous than the practice of trapping steam lines a hundred feet or more from the point where steam is used. Every foot of pipe that contains condensate is a foot of pipe that cools steam off and wastes coal! Get rid of the condensate where it forms, instead of at distant points, and cut down this waste! It requires more traps to do this, but the cost is comparatively light when your lines are fitted with the low-priced

STEAM TRAP SARCO

You can buy three Sarcos for the price of one bucket type trap, and by placing them where the condensate forms, you can draw it off instantly, instead of allowing it to drain back through enormous lengths of pipe, chilling the live steam in its progress.

Despite its small size, the Sarco is a little giant for performance. It drains the condensate off as rapidly as it forms, returning it instantly to the hot well without loss of heat units.

Many engineers have marvelled at the simple but scientific construction of the Sarco—the highly sensitive thermal element—the absence of complicated parts.

A 30 Days' Free Trial

will prove to you that the Steam Trap Sarco is a money saver. Quickly installed; does not require pit-digging or platform-building. Made in sizes ⅜ in. to 3 in., for any given pressure up to 200 lbs.

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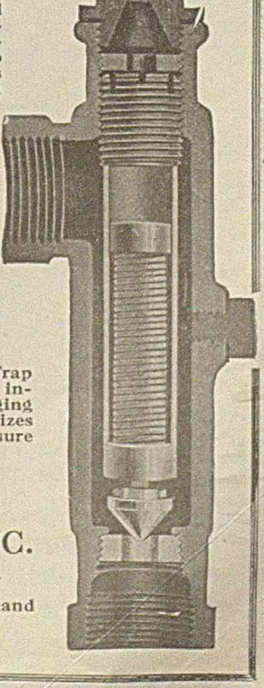
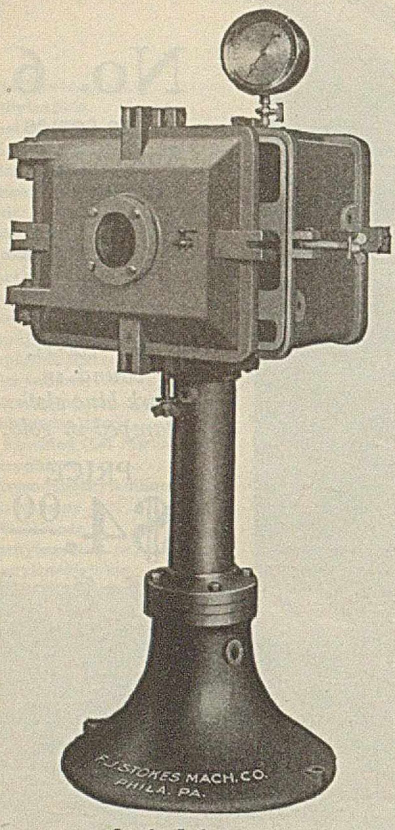
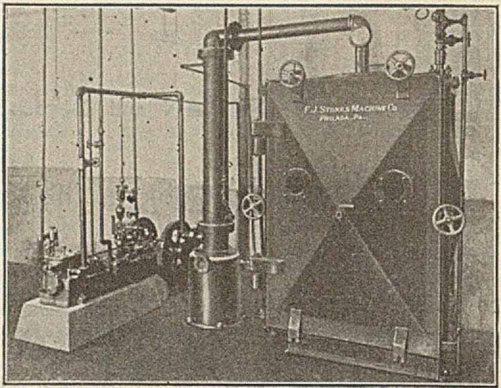


STOKES VACUUM DRYERS



In the Laboratory

In complicated organic processes laboratory control is essential.



In the Plant

The little Stokes in the laboratory will tell you how to run the big Stokes in the plant.

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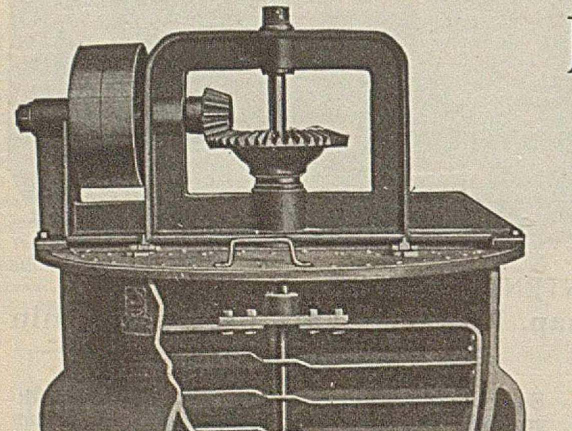
Philadelphia, Pa.

Make Every Penny Count



Style "J" Outside Sweep Agitator
Seamless—Leakless—Long Lasting
Guaranteed for Life

There was never a time when it was more necessary to make every penny count than right now.

Prosperity is "just around the corner" and the equipment you buy today should be the very best obtainable—so it can be depended upon to give uninterrupted service and produce real profits in the busy times just ahead.

Don't buy your jacketed kettles or mixers on a price basis. It does not take long for high upkeep and unreliability to outweigh low purchase price.

Dopp Seamless apparatus will give you satisfaction today and will go right on giving the same high degree of satisfaction for many years to come—some units we know of in constant operation for about 40 years and still doing their work as well as ever.

Sizes 1 to 1000 Gallons—an agitator for every mixing requirement, from thin fluids to heavy viscous substances.

Write for complete catalog No. 6.

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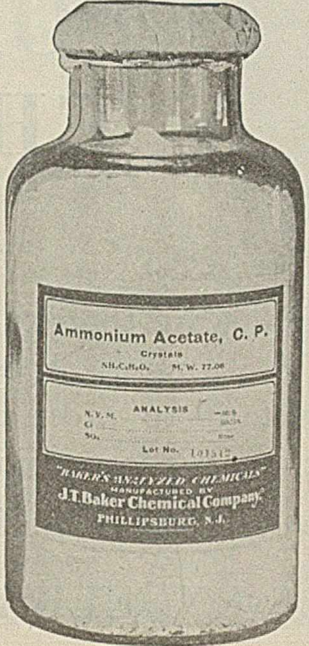
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