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EDITORIALS

A Fireside Chat

A friend in a somewhat philosophic mood recently remarked, "Some day when we are old men sitting before a memory-stirring fire on a winter's evening, we are going to look back upon this five-year period in American chemistry, and it will seem like a romance, with its recollections of intense efforts and speedy accomplishments, and its thrill of patriotic service." We agreed, of course. But while preparing to leave the old chair where five happy years have been spent we glanced over the scrap book containing the editorials from This Journal. These stirred our memory, and brought forth the conviction that it will not be necessary to wait until we are old men to get this sense of romance, this thrill of things accomplished. Draw your chairs up before the fire, the gas log, or the radiator, wherever in this broad land of ours you may be meeting the chill of this first touch of winter, and let's talk it over.

The story began in 1916 when consumers were suddenly faced with a cessation of imports of dyes. Do you remember the cry that went up from certain quarters, blaming the American chemist for not having a dye industry ready to meet the shortage, as if such a thing were kept in the ice box ready to serve when the cook is suddenly taken ill? Then, when an effort was made to begin manufacture of dyes and to secure protective legislation for the industry, propaganda, a word seldom heard at that time, showed its head in the shape of that industriously circulated but weird myth that dyes couldn't be made from American coal. That bird was soon shooed off that perch, only to light on the declared inability of the American chemist to make dyes. Again the bird has been dislodged.

Mr. Kitchin emasculated the legislation intended to safeguard the industry, but we believe Mr. Kitchin eventually regretted this, when he learned that Hugo Schweitzer wrote in detail to von Bernstorff how this impotent legislation guaranteed the eventual death of the American industry and recovery of the market by the German industry.

Nevertheless the industry has grown, filling more and more America's needs. With the development of gas as a means of warfare the industry has taken on a new and significant aspect. For this reason its safeguarding has been urged by former President Wilson, and more recently by General Pershing, Secretary Weeks, Secretary Denby, Secretary Hoover, Brigadier-General Fries, and Rear-Admiral Strouther Smith.

Let's go back again, now, to the time when the War Department, months after we had entered the war, felt that chemistry had no special part to play in warfare. Don't you remember the long up-hill fight that was required to keep the chemists from the Front, to avoid the very mistake that France and England avowedly so bitterly regretted? A whole year was required to force the conviction of the necessity of organizing chemists in a special branch of the Army. But the conviction finally came, and then was organized one of the most capable units in the world, the Chemical Warfare Service.

With the war over, retrogression immediately began; the Chemical Warfare Service was precipitously demobilized and the then Secretary of War and Chief of Staff got out their knives for the C. W. S. in the Army Reorganization Bill. Another fight was required and eventually won, when the Service was made a separate unit of the Army.

Read again the editorial, "Toluol, Toluol, and Then Toluol." Strange that, knowing full well the importance of TNT, and planning to raise an army of millions, we continued to burn the crude throughout the length of the land. Soon, however, the situation was completely changed.

Don't you remember the days when chemists were urging the conservation of platinum for government munition plants, and how the jewelers did oppose the effort? It was very thin ice on which the War Industries Board was skating, so far as platinum was concerned, toward the close of the war. There is still a remarkable story connected with this platinum campaign which some day may yet be told.

Perhaps one of the most far-reaching actions of this war period was the inauguration of lectures at West Point and Annapolis by distinguished members of the American Chemical Society. As the years go by the good effects of these lectures will make themselves felt more and more. We would prefer talking about the hopes of all of us for a successful outcome of the Conference on Limitation of Armament, now sitting, but so long as we must have any army or navy, these should be officered by men who understand the fundamental importance of chemistry in war making.

What about duty-free importation of scientific apparatus, glassware, and other tools used by the chemist? This is a subject that fascinates us from two points of view. First, confidence and inspiration are gained when it is remembered how quickly technical problems have been solved, thereby making available wares of the highest class of manufacture. Second, loyalty and foresightedness have been demonstrated in the way chemists have stood by the home manufacturer in spite of the allurements of duty-free importation privilege and depreciated foreign exchange.

Someone asks, "What has become of the Institute for Chemo-Medical Research?" Was the tone indicative of a belief that this movement has been forgotten? If so, you've missed your guess, old man. True, the Institute has not yet materialized, but we venture a prophecy—some day it will be an actuality! This confidence is based upon knowledge of the thorough report which has been prepared by the Committee at the request of the Chemical Foundation. It is now in the hands of the printer, and will be given wide distribution by the Foundation.

Let's not break up this chat without a few words about the chemist who is waking up to his responsibilities of letting his fellowman know something about what he is doing and how closely his work touches every phase and activity of life. That is the real miracle of the past five years. In accomplishing it there have been utilized the daily press, the magazines, popular books on chemistry, the Chemical Exposition, public addresses, and personal conversations. The response of the public has been fine and America is better off to-day because of it all—and that is the main point.

Now it's time to break up. The predetermined limits of space for this final chat tell us that closing time has come. We are not going to say good-by, for we are not going away, only going to work in another room of this house of our national welfare, a room into which many of you will some day enter. Here's hoping we may be able to be of some service in making that next room a place where you can show forth the best talent of the American chemist. It has been a great joy to work with you during these five eventful years. It will be a happiness to work for you during the years to come. And it is fine to know that during those coming years This Journal will be in the hands of one whose talents so fully qualify him for the work and whose devotion to the American Chemical Society is second to none. Here's Howe!

CHEMICAL INDUSTRY IN CHINA[1]

By William Henry Adolph

Shantung University, Tsinan, China

Rapid growth and changes in chemical industry in the United States in the last few years have been paralleled by developments of a similar magnitude in China and the other countries of the Orient which were only indirectly touched by the world war. The entire country has reacted rapidly to a number of stimuli, and has presented on the one hand a phenomenal growth in existing industries, and on the other hand a revelation of still more striking latent industrial possibilities. These stimuli have been partly the competition aroused by the aggression of other nationals in the country, and partly of a political nature connected with the prominence given the Shantung question at the peace conference.

Economic engineers have for some time projected industrial enterprise as a solution to relieve the effects of the tremendous population pressure in China. China has been essentially an agricultural country. The last two or three years have seen an enormous step in the direction of her industrial independence. The mysterious Orient is a thing of the past. During the space of a five years' residence in Shantung, the writer has made a number of notes which a certain professional duty seems to suggest should be passed on.

The developments in Shantung are typical of China as a whole. Shantung silk and peanuts have already immortalized the province. The Shantung silk, called *pongee* on the market, owes its peculiar qualities to the fact that the silk worms are fed on oak leaves, not on mulberry. Shantung hides and oils are rapidly coming to the fore. The causes which have held back these and other industries are twofold: one, a certain lack of trained technical experience on the part of the Chinese operators; the other, the failure on the part of foreign manufacturers of machinery—this trait is largely true of Americans—to study sympathetically the peculiar needs of the Chinese industry, and to design and adapt plant and machinery to the requirements of a less completely organized industry. America, not Japan, strangely enough, has replaced Germany in the affections of the Chinese industrialist. But we in the United States have not risen to our opportunity.

America may well take a lesson from Germany's methods in stimulating chemical industry in Shantung. Her expert studied the industrial needs of the province, designed machinery and plant of a type which was not used in Germany but which was needed in China. Our America houses too often have sent their catalogs and given up in despair when an order was not received by return mail. But the Germans cultivated the market, then patiently waited, taught, established industrial schools, were patient again, and built themselves into the good graces of the people. Even now the field is still a virgin field, and it requires expensive and rather tender cultivation on the part of the industrialist and commercial man. An enterprising peanut-oil producer knows perhaps how to run an oil press, but is unable often without help to order the machine he needs from the confusing specifications of an American catalog, and to instal it.

Americans traveling in China are astonished at the extent to which intelligent Chinese are looking to America as the source of new inspiration and help. In traveling through China, the writer found the simple statement that he was an American the most powerful password that could have been given. He was still more interested in observing the care with which his Chinese associate on industrial trips mentioned that the foreign visitor was an American. It invariably meant the doors were thrown open with a willingness. This was in spite of the fact that the Chinese manufacturer has preserved a good bit of his medieval reticence, and is cautious about imparting family trade secrets.

The situation in China divides itself into the recognition of two kinds of industries, with two kinds of industrial problems. In the first place are the old Chinese chemical industries, dyeing, glass, paper, etc., which had their origin in China's prehistoric days. In the second place are the chemical industries which are new to China, sulfuric acid, soda, tanning, which are now looked upon as the foundation stones of a modern chemical industry. It is these which have now to be founded from the very beginning.

The first, the old industries, will help fill some of the pages of our history of chemical industry, and will furnish some of the curious illustrations of how practice can race away from theory till theory is lost thousands of years behind. In China these were all small-scale industries, many of them family industries, and in most cases only supplementary to various phases of agriculture. They require a development that will enable them to retain their important position in the economic fabric of the country, and at the same time to satisfy the requirements of modern efficiency. The second, the new industries, involve serious financial problems as well as technical ones.

THE MADE-IN-CHINA MOVEMENT

The "made-in-China" cry which accompanied the recent patriotic movement has taken a real place in the life of the country, and it has not turned out to be but a fleeting enthusiasm. High-school graduates, and ex-soldiers whose experience has been limited to the manufacture of soda-water and vending of opium pills, have set up as chemical manufacturers, and the desire to *make*, instead of *import*, will gradually affect the status of our commercial relationship with China.

News came to us recently of a newly founded sulfuric acid plant in central Shantung, where pyrite was plentiful and fuel cheap; they were reported to be in difficulty. On arrival, our surprise was exceeded only by a certain amount of pathetic admiration. A couple of thousand dollars, all the money the investors possessed, had been expended in the erection of a small plant for the manufacture of sulfuric acid by the chamber process. There were four little lead chambers in a row, a pyrite burner was located at one end and at the other end was an outlet pipe for the excess gases. The manager, who was a high-school graduate and had studied a half year of chemistry in high school, stepped proudly forward, and explained that he had designed the plant unaided and that the completed plant was an exact copy of the diagrammatic sketch which was to be found in his high-school textbook. The plant had failed to produce satisfactory acid. The "company" was profoundly disappointed when shown that there were a number of important details which had been omitted in the crude sketch. This is not an isolated case of patriotic enthusiasm.

The "made-in-China" movement also manifested itself in other ways. A short time ago there was erected a high and imposing chimney, with the elements of a factory attached to its base. In a few days the chimney started

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[1] Received September 6, 1921.

spurting heavy nitric fumes, and simultaneously with the appearance of the fumes there were scattered broadcast over the Chinese republic handbills announcing the founding of a Chinese company for the manufacture of synthetic dyes in China to replace the imported variety. Patriotic Chinese dyers responded with enthusiasm; the new made-in-China dyes prospered with alacrity. The factory became the center of some interest, but visitors were not encouraged. An investigation showed that there were two doors in the factory. Into the east door were hauled on high single-wheeled barrows cases of imported dyestuffs. On the trip through the factory, the cases were opened, labels removed and changed for made-in-China labels, and the dyes were wheeled out the west door to parade as Chinese product. The yellow smudge which appeared from the stack was kept going constantly while the process of pasting on new labels proceeded.

RESUME OF CHEMICAL INDUSTRIES

It is possible to make only a partial list of the principal industrial items which are of interest to the chemist in China.

ALCOHOL—Very little industrial alcohol is manufactured in China. Alcoholic beverages have been used and prepared by the Chinese for ages. There is, however, a large variety of cheap materials aside from grains and sugar wastes which can be used in an alcohol industry.

BLEACH AND BLEACHING—A growing textile industry is demanding large quantities of bleaching powder and other chemicals which have not been used in the past. The new hair-net industry sends hundreds of pounds of old queues, cut off under the republican régime, to the United States to be bleached and dyed, and then has them shipped back to China for making into hair nets for the American market. The desire on the part of China to compete with foreign manufactured articles of all kinds calls for bleaching of the raw materials. The proper conditions exist for the establishment of an electrolytic bleach industry. No electrolytic industrial processes have yet been founded in China.

CEMENT—A few cement mills have been erected to take advantage of excellent raw materials. The Chinese sources of supply do not, however, fill the increasing demand for this and other building materials. Boshan, the ancient glass center in Shantung, is one of the centers where the cement industry would naturally be developed. The writer has examined many old structures and ruins of masonry which indicate that excellent concrete was used by the Chinese from very ancient times.

CHEMICAL FERTILIZERS—China is an agricultural country and several thousand years of intensive cultivation have exhausted the soil. Crops are raised only by the regular application of fertilizer. This consists principally of sewage, which is dried and marketed; its preparation forms the foundation of a widespread industry. In the absence of any sewer systems, it has been possible to make almost full return of the nitrogen to the soil. The rapid application of scientific methods to agriculture as well as modern principles of sanitation is beginning to demand the building up of a chemical fertilizer industry.

CHEMICALS. *Acids*—Pyrite is found in fair abundance in China, but sufficient capital and protection have not yet been united to insure a sound sulfuric acid industry. One large acid works has been in operation successfully for a number of years, and a number of others have been planned. No attempt as yet has been made to manufacture C. P. acids. The lead-chamber process is employed in all cases. Nitric acid is manufactured on a small scale.

Alkalies and Soda—Native soda and potash exist in China, but are failing to meet the heavier demands of modern industry. A number of LeBlanc soda works are being erected and conducted under the guidance of American trained experts.

Saltpeter—In a country so densely populated as China the accumulations of waste nitrogen in densely inhabited centers is considerable. A quantity of saltpeter is produced annually by scraping off the top surface of the ground in and around the dwellings and stables where this can be done conveniently, particularly in the country districts. The material is treated with wood ashes and extracted, and the potassium nitrate is allowed to crystallize.

Alum, Borax, Glauber's Salt, Green Vitriol, Copperas—A number of these fundamental chemical compounds are found native in China or have been manufactured by crude methods since ancient times.

DYES AND DYEING—China possesses and has used for centuries a large group of vegetable dyes, among them indigo, saffron, and a number of yellows, browns, and blacks. These the Chinese have used only in a very crude way, and some of them have been only partly studied, if at all. The fact that the Chinese have not developed their native dyes in a scientific manner is largely responsible for the present large demand for synthetic dyes from abroad.

Synthetic indigo had efficiently stamped out the native indigo which history indicates had its origin in Shantung, China, many centuries ago. The war revived the industry, which is strong in the north. It remains to be seen how the growing of native indigo, which has been on the increase, will survive under modern scientific management. German trade had done much to kill all of China's native dyes, but the war forced a certain return to the use of native dyes and to a certain extent forced the beginning of a scientific investigation of China's natural wealth in dyestuffs.

EGGS, DRIED ALBUMEN, DRIED EGGS—Chinese eggs are much smaller than American eggs and for that reason, in spite of their cheapness, they have not met with favor as fresh eggs on the American market. The price of eggs in China has risen considerably during the last decade, till they now cost about 5 or 6 cents (U. S. currency) per dozen in the egg-producing districts. The dried egg industry has flourished in China for about ten years. The egg is dried in zinc pans whole, or the yolk and albumen may be dried separately. The U. S. Customs requirement, dating from a few years ago, that the zinc content must be less than 0.1 per cent, almost killed the industry, but it recovered with the introduction of the newer method of spray drying. The lay of Chinese hens in Shantung province is higher than the remainder of China, said to be due to the fact that Shantung chickens are fed soy beans, which contain a high percentage of protein. An opportunity exists for the use in China of this large supply of cheap albumen. Attempts have been made to develop the manufacture of artificial ivory, and similar products.

GLASS—Glass has been manufactured in China from prehistoric times, and in the two or three centers where it has been carried on essentially the same methods as were employed in ancient days are now used. Window glass is also manufactured, and improvements are gradually being introduced. One of the first constructive steps furthered by the Germans in Shantung was the establishment of a large glass works. They employed a large staff of Belgian experts to train the Chinese workmen. This particular works was closed in 1914.

MATCHES—The Chinese were quick to see the advantage of matches over flint and steel, and one of the first of the smaller modern industries to flourish was the manufacture of matches. The white phosphorus and other chemicals required are imported, and sometimes the wooden sticks and boxes also, the only cheap materials being the labor involved. The imported phosphorus is in turn derived from bones originally exported from China.

METALS AND MINERALS—It was the reports of China's fabulous mineral wealth which first drew the attention of the Occident, and it is the mining industry which is seeing the gradual disappearance of traditional unscientific methods. The old method of developing mines in China is well illustrated by the story of the founding of the Hanyang Iron Works. The machinery and equipment for this were ordered by an enterprising old viceroy, who knew neither where he was going to locate the plant nor the kind of ore it was to handle, for the ore had not yet been discovered. When he ordered the outfit he was stationed in Canton, in south China; when the machinery arrived, he had been transferred to central China. It was a piece of remarkable good fortune that ore suitable for the type of plant which he had ordered was soon found at his new post, Hankow, and that a coal mine to furnish fuel for running the plant was found nearby.

The mining industry of China for many years was largely a contest between enterprise and the desire of officialdom to share in the profits. Actual prejudice and superstition were not such important factors as often imagined; but successful mining has depended upon the clever manipulation of legal as well as other kinds of machinery.

All the common metals and minerals are found in China, with the exception of any appreciable quantities of gold or petroleum. The mineral wealth of Shantung was largely responsible for Germany's decision to make that her sphere of influence. Those which have drawn considerable attention during recent years are:

Coal—The coal reserves of China half a century ago were estimated to be limitless. Saner surveys now place the figure at about the same as that for the United States; moreover the coal is found in every province, not simply in favored areas. The annual output is at present about one-thirtieth of that in this country. Shantung province does not possess as much coal as it did in Germany's dreams. There are very large deposits of anthracite in China as well as all other varieties. China has just entered upon the role of coal exporter to Europe. The production for 1920 totaled 13,000,000 tons, of which over one-half was anthracite.

Iron—The glowing reports of von Richthofen, Germany's early scientific emissary to China, which told of unlimited reserves of iron ore have also been shown by careful studies to be erroneous. The present estimates place the workable iron reserves at 400,000,000 tons. The production of iron per capita in China is only one-three hundredth of that in the United States.

Antimony and Tungsten—China furnished the world with antimony and the production was stimulated tremendously by the war. Tungsten ore was likewise developed, but the rise in exchange and the attempt of official interests to tax the profits killed this industry and seriously crippled the antimony trade.

PAPER—Hand-made paper has been in use for centuries. The paper, however, is of inferior grade, and does not seem to have shown any improvement during the course of the centuries. Only one modern paper-mill complete with calender machines exists, and this uses old rags as the sole raw material, of which there is an abundant supply in China. The product of this mill has difficulty in competing with imported paper, but the difficulty probably lies, like many other Chinese industrial difficulties, in inefficient management. The future of the paper industry seems to depend upon the discovery of a new Chinese raw material. This is bound up with the fuel question, for all grass and weeds are at present used for domestic fuel and heating; wood, except the bamboos of the south, is too expensive or nonexistent.

POTTERY—China has excelled in the production of glazed ware and porcelain, but the industry still remains on much the same basis on which it has rested for many centuries. The country possesses excellent raw materials, and a number of recent attempts have been made to produce fine heat-resistant porcelain for modern laboratory use, but without marked success.

SALT—The production of salt has long been a government monopoly, and the salt tax is one of the government's principal sources of income. The high duty has hindered the development of industries using salt as a raw material. Salt is mined, and brine, both from wells and sea water, is evaporated by solar evaporation. The ancient salt wells of western China, many of them 2500 to 2800 feet deep, are one of the industrial curiosities of the Far East. Use is even made of the salt bittern or mother liquor, which is sold for use as a coagulant in the manufacture of vegetable cheese.

SOAP—In many places in interior China, the Chinese have used varieties of vegetable soap. This is derived usually from a soap bean and contains principles identical with or similar to saponin. The manufacture of soap sprang up all over China with the introduction of the principles of modern chemical industry, and American and European imported soaps are now meeting serious competition. Crude methods are in many places still employed and the products placed on the market are often of doubtful value. There is need for an experienced and well-trained personnel in developing this industry.

SOY BEANS—The soy bean of north China not only is the source of the bean oil which is now the leading article of China's exports, but is the source of numerous other products. The press cake is being used for fertilizer on the rice fields of Japan and seems to meet a special need there which cannot easily be replaced by other varieties of fertilizer. The only serious question to China is that it means the annual shipping out of the country of large amounts of protein material which China should have for use at home. A movement is on foot to make use of the casein which can be prepared from the soy bean and to turn it into a product like the American bakelite.

SUGAR—The cane-sugar industry has been long established in south China, and the beet-sugar industry has just recently been established in Manchuria and Shantung. Considerable progress remains to be made in the methods for refining the finished product.

TANNING—Cattle raising and the production of hides is a growing industry in north China and Mongolia. The old method for curing leather was not tanning at all. The word "American leather" during the last decade had come to be synonymous with the word for good leather, and the new move to establish home industries included the demand that China's hides must be tanned at home. This is far from being accomplished, but rapid progress is being made. Chrome leather is now produced successfully, and the other processes are gradually being put into operation. The need is for trained and experienced leather men.

VEGETABLE OILS—The oil industry in China includes: castor oil, cottonseed oil, peanut oil, sesamum oil, soy-bean oil, tung oil (China wood oil). These oils have long been produced and fill certain domestic needs. The progress of the last few years has meant little else than the extensive substitution of modern machine presses for the old-time crude and clumsy wedge devices for squeezing the seeds till a fair amount of the oil was expressed out. Practically no study has been made in China of the refining and proper standardization of these oils for the industries. Many of the oils will ultimately be worked up into their various products with profit before being exported. No paint industry has yet been developed. All good paint is imported, though all the necessary raw materials exist in the country for a prosperous industry. The Chinese have been satisfied in the past with a few kinds of good but extremely expensive lacquer, and with poor types of varnishes and paints made from oils which at best were only semi-drying oils. The improvement of the tung-oil industry starts with the growth, selection, and improvement of the tung tree.

CONCLUSION

The writer is anxious to urge that the chemical industries of China need our sympathetic interest in their development, and also a goodly amount of American capital. The industrial situation is characterized by cheap labor, and by a surprising manual skill and power of application on the part of the Chinese workman.

This open door is an industrial one; it is not merely a political phrase. In spite of ourselves, American interests are being dragged into the China field. American locomotives in increasing numbers are appearing on the Chinese railways. It is significant that not we, but our American-trained Chinese students, are putting them there.

One is impressed by the fact that the discussions of industrial problems which appear in the journals of this country are so easily limited to the boundaries of the United States; on very special occasions they may be extended as far as Alaska or the Philippines. Astounding revelations of the ignorance of technical men in the United States upon the needs and problems of the industrial world abroad crop up. A few years ago an American consulting engineer who pretended to cater to the oriental field and who was anxious to keep us in China supplied with all the catalogs and literature on the latest types of machinery, sent a supply of pamphlets expounding the virtues of a new device which was just appearing on the market—a stump-puller. His machine might have been used in clearing the primeval forests of central Africa, but Shantung had been for so many treeless centuries in the grip of floods and famines, with mountains bare and every inch of soil under such intensive cultivation, that we could have desired nothing so much as a single stump to pull. There are frequent evidences of our lack of information on the geography of the districts abroad which we plan to serve in a technical capacity.

VITAMINE SYMPOSIUM

Papers presented before the Division of Biological Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

Factors Influencing the Vitamine Content of Foods

By R. Adams Dutcher

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Probably no phase of the vitamine question is attracting greater attention at the present time than that which has to do with the vitamine content of our natural and prepared foods and feeding materials. Hardly a week passes that the writer does not receive letters from teachers, housewives, dairy-men, and manufacturers, asking for advice regarding the effect of this or that process of food treatment upon the vitamine content of the particular article of diet in which they are interested. It is difficult, if not impossible, to answer many of these questions satisfactorily for the reason that many of the problems have not been investigated and many of those which have received attention have been influenced by so many factors that it is difficult to say with any degree of certainty what the real facts may be.

In a paper of this type it is impossible to do more than point out what seem to the writer to be some of the outstanding phases and to emphasize some of those factors which seem to be of the greatest importance.

FOODS OF PLANT ORIGIN

It is quite clear that fresh undried cereals possess antineuritic and antiscorbutic properties that are not manifest in the dried seed. While the antineuritic vitamine occurs more or less abundantly in the dried cereals, it is found that the antiscorbutic vitamine has practically disappeared during the drying process.

When seeds are allowed to germinate,[1,*] however, it is found that they possess marked antiscorbutic potency and their value with regard to the antineuritic vitamine has been enhanced to some extent. The British military authorities[2] have made use of this fact by requiring the use of sprouted beans as an antiscorbutic food for certain of their expeditionary forces.

Steenbock[3] argues that most plant tissues, which are characterized by the production of carotinoid pigments, are relatively rich in the fat-soluble vitamine. He is of the opinion that these pigments are very closely related to the fat-soluble vitamine or are identical with it. Palmer,[4] Drummond and Coward,[5] and Stephenson[6] do not hold this view and cite experimental evidence to disprove Steenbock's generalization.

The relationship between metabolic processes in the plant and the production of fat-soluble vitamine is not at all clear, and the fact that plant leaves are rich in this accessory factor has caused considerable speculation. Some writers maintain that the vitamine is a result of or associated with metabolic processes. This is supported by the fact that the vitamine content of plants such as the carrot[7] and alfalfa[8] seems to be at its maximum during the early stages of growth, when the plants are young and when metabolic processes are most active.

It must be of considerable satisfaction to the botanist to know that the animal kingdom is dependent upon the plant world for vitamines as well as the other nutrient materials. It appears to be quite evident that the animal body cannot synthesize vitamines, at least to an extent where they can be considered of dietary importance.

FOODS OF ANIMAL ORIGIN

There are undoubtedly four factors operating to influence the vitamine content of fleshy foods: (*a*) The diet of the animal previous to slaughtering, (*b*) the type or species of animal, (*c*) the type of tissue used as food, and (*d*) the method of food treatment.

With reference to the first factor, *i. e.*, the diet of the animal, the evidence points to the fact that the vitamine content of body tissues must, of necessity, be influenced by the vitamine content of the diet. Drummond and his co-workers[9] have shown that lard does not usually contain the fat-soluble vitamine, owing to the fact that the ration of the

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[*] Numbers in text refer to Bibliography, p. 1104.

hog is invariably deficient in this particular food factor. This is a partial explanation for the differences in the body oils of different types of animals. That the vital organs of the type represented by the liver and the kidney are rich in vitamines A and B scarcely needs comment. Food treatment will be discussed later in this paper.

When we consider dairy products we are confronted with a similar situation. While milk is undoubtedly one of our very valuable foods in this regard, it is possible to produce milk which is almost devoid of vitamines. At its best, milk cannot be considered an antiscorbutic food unless it is consumed in quantity.

In our work at Minnesota,[10] we have shown that milk may be relatively rich or very poor in antiscorbutic potency, depending upon the vitamine content of the cow's ration. Our work indicates, also, that the antiscorbutic properties of milk are most easily affected by feeding, although Dr. Kennedy has collected data which show that the fat-soluble factor is also susceptible of considerable fluctuations, which appear to be seasonal in ordinary dairy milk. We are now preparing data, for publication, which show that rats will grow normally when the fat-soluble vitamine is furnished by a ration containing 5 per cent of butter obtained under ideal feeding conditions. On the other hand, we have been unable to obtain normal growth when this vitamine is furnished by a ration containing 20 per cent of butter fat produced on a vitamine-poor ration. We have found, also, that 10 cc. of milk, produced on vitamine-rich rations, will usually furnish sufficient vitamine A and vitamine B for normal growth, while larger quantities of milk, produced on vitamine-poor rations, were very deficient in both of these food accessories.

In addition to seasonal variations in the vitamine content of milk, we have observed marked effects of climatic conditions. Periods of drouth, followed by browning of the pastures and drying of the grass, are reflected in the growth curves of the experimental animals. These results are in agreement with those which were obtained in a similar study on the antiscorbutic vitamine. Other investigators have reported similar observations.[11] It is quite evident that the water-soluble (B) vitamine does not fluctuate to any considerable extent, on account of the fact that most dairy animals receive some grain. This is not true for all dairy stock, however, for the writer has seen cattle go through the winter on some western farms on a diet composed very largely of straw. There is little wonder in such cases that the animals have a rough, unthrifty appearance by the time the spring months arrive. Certainly the milk and butter from such animals must be almost devoid of vitamines. It may be said, for the benefit of Dr. Steenbock, that our vitamine-poor butter was practically colorless. These observations on the influence of diet are of far-reaching significance, not only in commercial dairy production but with reference to the intelligent feeding of all lactating animals. Furthermore, intelligent feeding in the dairy industry means not only higher production but more nutritious milk and butter.

No systematic investigations have been made relative to determining the best winter feeds to employ for the production of vitamine-rich milk. Silage does not appear to enrich milk as far as the antiscorbutic vitamine is concerned. We have observed that good, green alfalfa seems to improve the nutritive value of the milk, but in just what way we are not prepared to say. There is every reason to believe that the nutritive value of eggs may be influenced by feeding. The practice of feeding sprouted grains to poultry during the winter months should produce eggs containing increased amounts of both the fat-soluble and water-soluble (B) vitamines.

The Influence of Food Treatment

Very little has been published concerning the influence of chemical environment upon the stability of the vitamines A and B. It is apparent that the antiscorbutic vitamine is fairly stable in an acid environment,[12] while it appears to be less stable to alkalies.

As a rule foods seem to lose their vitaminic activity during long periods of storage. Just what factors are operating under such conditions, it is difficult to say. Certainly oxidation must be considered.

Many desiccated foods appear to have lost their activity during the drying process, while others have not. There are several factors to be considered in this regard. First of all, not all investigators work with the same quantities of material in their feeding trials. In the second place, the original vitamine content of the desiccated food must be taken into consideration. Unless such materials are fed at the lowest level, in the fresh condition, it is conceivable that, although vitamine destruction takes place, there may be a sufficient quantity remaining to supply the experimental animals adequately. Discrepancies in the literature may be explained, quite often, on this basis.

Often temperature studies cannot be depended upon owing to the fact that oxidation factors have been ignored. Hopkins,[13] Hess,[14] Zilva,[15] Drummond and co-workers,[16] and others have shown that the fat-soluble and antiscorbutic properties of foods are destroyed by oxidation. Our own work supports this. Edla Anderson, working in the writer's laboratory, has shown that oxidation destroys the antiscorbutic value of milk, while pasteurization in closed vessels or boiling does not affect the milk appreciably. Her results indicate, also, that high temperatures for a short time are less destructive than lower temperatures for longer periods. Harshaw and Hall, also working in the writer's laboratory, have shown that orange juice loses its potency in the presence of hydrogen peroxide, even at room temperature. Boiling, however, in the absence of hydrogen peroxide does not appear to have a harmful effect. Heating in the presence of hydrogen peroxide hastens the oxidative destruction.

Mr. Ackerson, one of the author's students, constructed a milk-drying apparatus in which milk was dried in an excess of hot air. The milk particles during the drying were not subjected to a temperature exceeding 110° C. The temperature of the box did not exceed 120° C. This milk powder was valueless as an antiscorbutic food, although the same quantity of raw milk possessed some antiscorbutic potency. No detailed studies, so far as the writer is aware, have been made in this regard, on the effect of drying and curing of hay and, for that matter, many human foods.

A prominent dairy authority informs the author that his observations have led him to the belief that there is considerable fluctuation in the nutritive values of hays grown on the same land from season to season. He is of the belief that the conditions of drying and curing are very largely responsible for these differences, although the maturity of the plant at the time of cutting must be considered. Practical feeders have observed that bright green alfalfa, properly dried and cured, is superior to the light colored crops, bleached out by unsatisfactory climatic conditions or careless agricultural practice. Careful investigation of the vitamine content of the leafy hays produced under various conditions of drying and curing should yield information of scientific and practical importance.

No comprehensive work has been done upon the changes in the vitamine content of silages of various kinds in comparison to the vitamine content of the fresh agricultural plants from which the silages are made. This information is badly needed in order that the winter ration may be of the highest nutritive value. Good as our winter rations, containing silage, are known to be, the fact remains that winter-fed cows respond to pasture feeding, in the spring, out of all proportion to the caloric value of the green grass ingested. The animals invariably respond in milk production, physical condition, and smoothness of coat. Investigations of our winter dairy rations should assist in improving this situation. Similar studies should be made on many of our commercially prepared foods.

It has already been indicated that heat undoubtedly possesses a destructive action but oxidation seems to be an equally important factor. Drummond[9] and his co-workers point out that this is one reason why lard is usually devoid of vitamine A. They contend that the small amount of vitamine that is normally present in lard is destroyed in commercial rendering processes.

In the light of our present knowledge, proper desiccation, with a minimum of air and a high temperature for a short time, should be advantageous. We have little or no knowledge of the influence of humidity, acidity, alkalinity, concentration of sugars, etc., during the drying process.

Some investigators find no antiscorbutic value in certain condensed milks. Hume[17] reports that condensation by the vacuum pan method had no effect upon the antiscorbutic properties of a sample of milk under investigation at the Lister Institute. Professor Combs, Miss Francis, and the writer are now investigating this question further, at the Pennsylvania State College. We are making several types of condensed and evaporated milks by means of the Ruff evaporator, which employs a blast of air through the heated milk. We are comparing the vitamine content of this milk with the fresh raw milk and with the same milk condensed in a commercial vacuum pan.

As far as vitamine destruction is concerned, we have little to fear in our ordinary cooking processes unless the length of time of cooking is excessive. The water-soluble vitamine seems to be more stable to heat than either of the others, although it is destroyed by long-continued heating or by autoclaving. Even when some vitamine destruction occurs, there is every reason to believe that there is seldom danger of a vitamine deficiency. Neither is there much to fear in commercial pasteurization of milk, provided the usual method of vat pasteurization is employed. Granting that some vitamine destruction takes place in many of our commercial processes, there seems to be no reason for being unduly disturbed, providing the diet is not restricted, for long periods, to foods thus treated. Such foods are of great value and their manufacture must not be discouraged. We must simply recognize their deficiencies and supplement these deficiencies with other foods. Our work on milk also lends support to the practice of "short-time boiling" of milk advocated by Lane-Claypon[18] and many pediatricians.

We must admit that our investigational methods are far from satisfactory. Our best planned work in many instances is only roughly quantitative, but the results obtained in the ten or twelve years of vitamine research have repaid their financial cost many times.

The applications of vitamine research to the feeding of malnourished children in Europe, and especially in Vienna, by Miss Chick and her co-workers, is one of the best examples of the practical value of this branch of nutritional science.

BIBLIOGRAPHY

1—V. Furst, *Z. Hyg. Infektionskrankh.*, **72** (1912), 121; H. Chick and E. M. Delf, *Biochem. J.*, **13** (1919), 199; B. Cohen and L. B. Mendel, *J. Biol. Chem.*, **35** (1918), 425; J. F. McClendon, *Ibid.*, **40** (1919), 243.

2—H. W. Wiltshire, *Lancet*, **1918** [II], 811.

3—H. Steenbock, *Science*, **50** (1919), 352; H. Steenbock and P. W. Boutwell, *J. Biol. Chem.*, **41** (1920), 81, 163; **42** (1920), 131; H. Steenbock and E. G. Gross, *Ibid.*, **41** (1920), 149.

4—L. S. Palmer, *Science*, **50** (1919), 501; L. S. Palmer and C. Kennedy, *J. Biol. Chem.*, **46** (1921), 559.

5—J. C. Drummond and K. H. Coward, *Biochem. J.*, **14** (1920), 668.

6—M. Stephenson, *Biochem. J.*, **14** (1920), 715.

7—A. F. Hess and L. J. Unger, *J. Biol. Chem.*, **38** (1919), 293.

8—T. B. Osborne and L. B. Mendel, *J. Biol. Chem.*, **39** (1919), 29.

9—J. C. Drummond, J. Golding, S. S. Zilva and K. H. Coward, *Biochem. J.*, **14** (1920), 742.

10—R. A. Dutcher, C. H. Eckles, C. D. Dahle, S. W. Meade and O. G. Schaefer, *J. Biol. Chem.*, **45** (1920), 119.

11—E. B. Hart, H. Steenbock and N. R. Ellis, *J. Biol. Chem.*, **42** (1920), 383; A. F. Hess, L. J. Unger and G. C. Supplee, *Ibid.*, **45** (1920), 229.

12—A. Harden, *Lancet*, **1918** [II], 320; E. M. Delf, *Biochem. J.*, **14** (1920), 211; V. K. LaMer, H. L. Campbell and H. C. Sherman, *Proc. Soc. Exptl. Biol. Med.*, **18** (1921), 122; A. F. Hess and L. J. Unger, *Ibid.*, **16** (1919), 52.

13—F. G. Hopkins, *Biochem. J.*, **14** (1920), 725.

14—A. F. Hess and L. J. Unger, *Proc. Soc. Exptl. Biol. Med.*, **18** (1921), 143.

15—S. S. Zilva, *Biochem. J.*, **14** (1920), 740.

16—J. C. Drummond and K. H. Coward, *Biochem. J.*, **14** (1920), 734.

17—E. M. Hume, *Biochem. J.*, **15** (1921), 163.

18—Janet E. Lane-Claypon, "Reports to the Local Government Board on Public Health and Medical Subjects" (London) (New Series **63**).

Standardized Methods for the Study of Vitamines

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The enormous amount of work that has been reported in the past few years upon studies relating to the vitamines has brought about a marked increase in interest in some lines of biological and food chemistry. As one carefully studies the many scientific papers on vitamines, he is impressed with the idea that the general plan of carrying out the investigations has been more or less characteristic or provincial with certain laboratories. That is, there is often such a difference between the basic plans for executing the experiments that the results of similar studies reported by the several workers are generally not comparable. It is, therefore, evident that the conclusions will not be consistent at times, and also that a certain amount of confusion as to the relative vitamine content of this or that substance will be produced.

It is natural perhaps that such a condition of affairs should have arisen. For as long as we know so little about the chemical nature of the vitamines, and our chemical methods for isolating them are so meager, we must of necessity be dealing with extracts which are a mixture of substances. Then, too, having to rely upon the biologic feeding method, where the animal, food and environmental conditions should be under exact control, one readily realizes how fundamentally important and how difficult it is to obtain accurate results at all times. It is thus easy to see that unless there is some definite understanding as to details of procedure, many variables may probably be introduced by each laboratory working on the subject.

To the writer's mind, it is imperative that something should be done to modify this condition; otherwise what is being reported upon the vitamine content of such substances as foods and vitamine products will need to be revised very considerably later on. These statements are not intended to imply in the least that the results thus far obtained are not of extreme value.

Considerable time and effort have been put forth to devise quantitative methods for measuring the vitamines in extracts made from foods. Various forms of animal and plant life have been employed. Thus, Emmett and Allen[1,*] tried the tadpole; Chambers,[2] the paramecium; and Williams[3] and Bachmann,[4] the yeast. The yeast method as suggested

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[*] Numbers in text refer to Bibliography, p. 1106.

by Williams for measuring the antineuritic vitamine has shown the most promise.[5] However, the objections to it that have been put forth are of such a nature that it would seem that further reports will be needed before the desired confidence can be placed in it.[6]

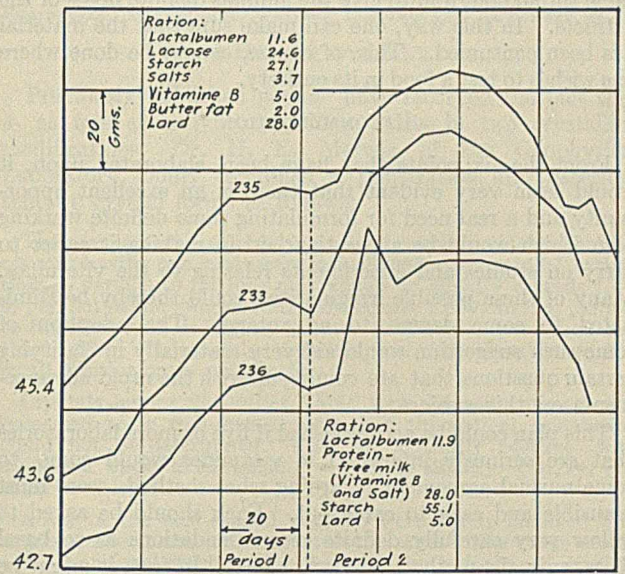

Fig. 1—The curves show how one may be misled by changing too many factors in the diet and then not running the test over a long enough time. The diet in Period 1 was slightly below the normal for growth, being low in fat-soluble A. In Period 2 for the new diet, all the fat-soluble A was left out, the amount of starch was increased, the fat was reduced, and new sources of water-soluble B vitamine and mineral salts were used. The rats began to gain following the change, instead of making the expected decline. This was undoubtedly due to the alteration in texture and palatability of the diet. Later, after 35 days, the rats lost in weight and developed the usual symptoms of xerophthalmia, etc. Similar conditions might result if one food were substituted for another in part or whole.

We are, therefore, still forced to rely upon the more laborious biologic method, which involves the feeding of animals, as the most dependable and safe guide. In fact, for some time, apparently, this method will have to be resorted to in the last analysis where any reasonable doubt exists.

In view of this fact, the suggestion might, therefore, be made that we endeavor to adopt a plan whereby it would be feasible to profit by the very valuable work done thus far and to carry out a series of coöperative feeding experiments so as to establish a more uniform scheme for the study of vitamines. This should be done with the idea of working toward standardizing some methods which in turn could be adopted provisionally. From the experience gained in working along nutritional lines for over fifteen years, the past five of which have been devoted to vitamines in particular, it would seem to the writer that there is much to be gained by following out such a program. It would serve as a helpful guide in determining when one has acquired sufficient knowledge of the technic to feel confident of the accuracy of his results. In this way alone it would be of great value to research workers and to the control departments of some of our industrial laboratories.

Points to Be Considered

In line with this suggestion a few points may be brought out to emphasize this need and point to some plans that might be considered:

1—There should be a strict uniformity in the basal diets. Thus, in the case of the growing rat, we should agree upon a basal diet that is complete for normal growth and reproduction; upon one deficient only in the water-soluble B vitamine, and upon one deficient only in the fat-soluble vitamine or vitamines. And in the case of the guinea pig, we should have a complete basal diet and one deficient in the water-soluble C. In these diets, it should be understood that the percentage of protein, carbohydrate, fat and mineral salts, and the kind and quality of these nutrients should be the same throughout, for the particular purpose intended. That is, all laboratories should use exactly the same basal diets.

It would then be possible always to employ these rations for the normal and pathological control groups and then to compare with these control findings, the results obtained from any other combination of nutrients that seemed desirable in connection with a particular phase of a vitamine project that one might have under way. That is, if the control data obtained from these basal diets were always reported along with the experimental results, it would be easier to interpret and compare the conclusions from different workers.

2—In the preparation of these basal diets, definite methods should be outlined, with respect to detailing just how to purify the various constituents used—the proteins, carbohydrates, fats, and mineral salts. Besides, exact methods should be given for preparing the vitamine extracts that are to be incorporated. Then again, it should be stated clearly how and in what order these ingredients are to be combined; for unless this is done the texture of the ration will often vary considerably, and thereby an unintentional error will be introduced which might affect the food consumption, and this in turn might influence the trend of the weight curves, etc.

3—It is equally important that there be some definite statements made with respect to the experimental animals. In the case of rats and guinea pigs, the age, weight, sex, and exact physical conditions should be carefully observed and stated. It is known, for example, that, for the best comparisons, the animals should be of about the same age and weight at the start, and that younger rats are preferable to older ones. In our own work where we have used some 2000 pigeons, we find that it is necessary to consider breed, previous feeding, age, body conditions, weight, season of the year, etc., in order to obtain the best results in testing for the antineuritic vitamine.

Also, in the case of handling and taking care of the animals, it is essential to bear in mind that one should avoid exposing them to sudden changes in temperature and to undue excitement, and to too much handling. Systematic attention should be given to cleaning and disinfecting the cages, bedding,

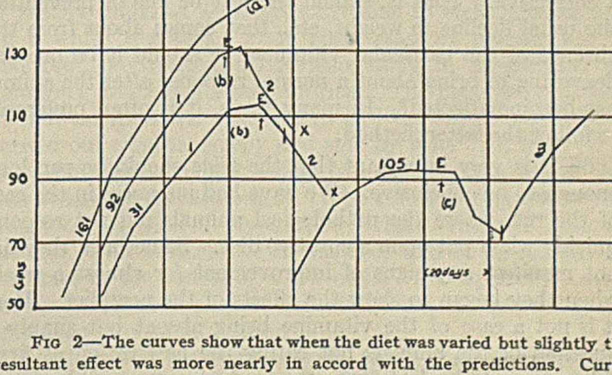

Fig 2—The curves show that when the diet was varied but slightly the resultant effect was more nearly in accord with the predictions. Curve *a* contained all the nutrients for normal growth. Curves *b* lacked the fat-soluble A vitamine. In the latter part (2) of this curve, fat devoid of this vitamine was introduced by substituting it for an equal amount of lard. No change occurred. Curve *c* also lacked the fat-soluble A, but later the fat was introduced which contained this vitamine. Increased growth took place along with the correction of xerophthalmia.

food cups, and water receptacles. Vermin or lice should be scrupulously excluded. Special care should be given an animal when it becomes appreciably affected by the deficiency disease, and so on. In fact, it is only after considerable experience that one can always be sure the effect of the experimental diet is a bigger factor than some of the other variables that may have been introduced.

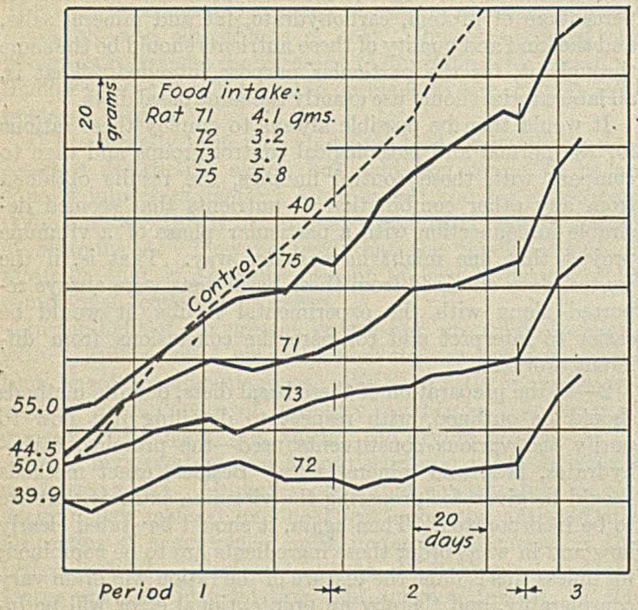

FIG. 3—The curves illustrate how it is sometimes necessary and essential to correlate the food intake with the weights. Here the weight curves followed almost in the same relation as the food intake. Rats 71 and 75 ate the most, and gained better than rats 72 and 73 which ate less.

Similar results were obtained by Osborne and Mendel[7] in feeding raw and cooked soy beans. The rats practically declined to eat the raw food and hence made no gains, while they ate the cooked food readily and grew normally.

4—It is very important to state whether the animals are to be force-fed or not; whether the food-intake is to be accurately recorded or not; whether the rations are to be made frequently or in large enough quantity to last for a considerable time; whether the consistency of the food or ration is appreciably altered when the changes in the diet are made, and, if vitamine extracts are to be used, whether the animals are to be treated during the test period, or fed at this juncture a mixture of the basal diet and the extract.

5—In the feeding, the question arises whether the rations should be tested from the standpoint of a prophylactic or a corrective. That is, should the test be one of preventing the usual decline in weight, etc., that comes about from the absence of the particular vitamine, or should it be one endeavoring to bring about a normal response after the animal has become affected? In many ways, it is often preferable to follow the latter method.

6—It is very important that the tests should be run long enough to be conclusive. We have had instances in the case of the rat, where the pathological animals did not respond quickly when put upon a curative diet. Sometimes they did not manifest any signs of improvement for almost a week, when they began to show the effects of the new diet. Here it is not a case of the vitamine being absent but simply a question of the animals not eating the new ration at first. When they do begin to take the food, the effect of the treatment will become very evident. However, the precaution should be taken to make sure that any gains in weight are not due simply to a change in the physical nature of food, rendering it possibly more palatable. Noting the physical condition of the animal and continuing the test long enough will settle this point. Where it is possible, as in using extracts, it is generally much better to keep the basal diet the same throughout and to give the animals definite doses of the extracts. In this way, one can make sure that the material has been consumed. This, of course, cannot be done where one wishes to test a food in its entirety.

RECOMMENDATION

From the six points that have been elaborated upon, it would seem very evident that there is an excellent opportunity and a real need for formulating some definite working plan which would be a practical aid in making it easier to carry on studies and experiments relating to the vitamines. Many of these possible irregularities could thereby be eliminated to some degree to advantage. The adoption of some such suggestion would aid very materially in clarifying certain questions that are coming up with the rapid advancements on this subject.

This plan could be accomplished if five or more laboratories that are seriously interested in vitamines would come to some mutual agreement regarding what methods seem most plausible and easy to carry out. Each should be asked to follow very carefully definite recommendations as to basal diets, animals, methods of feeding, etc. In fact, it might be best to go still further, in the beginning, and make up a large supply of the basal rations and to send portions to each investigator to use in accord with certain directions. In turn, the results obtained could be collected and studied to determine how closely the laboratories agreed.

These data would be of immense value and they might immediately settle and help to establish some very essential and fundamental facts. For one thing, the results would make it possible to determine what allowance should be made for the technic and personal factors that enter in. Also a number of points as to the exact pathological conditions that are brought about could be more clearly established.

Having thus obtained some fair knowledge of the range of experimental expectation that one may figure upon, it would then be possible to elaborate the procedure in any way that the individual project might suggest. However, even then the number of variables introduced at any stage in the experiment should be few enough and in such sequence that proper deductions would be possible.

This plan would seem to be a logical one at this stage in the development of the subject. It would be to the best interest of those who are in charge of research and control work on vitamines; it would help to add greatly to the valuable facts that are already at hand on the etiology and pathology of the deficiency diseases; it would make it possible to come to a much more definite conclusion as to what foods or food products are rich or poor in certain of the so-called vitamines, and would assist appreciably, in general, in obtaining fairly definite relative values.

BIBLIOGRAPHY

1—A. D. Emmett and F. Allen, *J. Biol. Chem.*, **38** (1919), 325.

2—M. Chambers, *Biol. Bull.*, **36** (1919), 82.

3—R. J. Williams, *J. Biol. Chem.*, **38** (1919), 465; **42** (1920), 259.

4—F. M. Bachman, *J. Biol. Chem.*, **39** (1919), 235.

5—W. H. Eddy and H. C. Stevenson, *J. Biol. Chem.*, **43** (1920), 295; C. Funk and H. E. Dubin, *Ibid.*, **44** (1920), 487; F. K. Swoboda, *Ibid.*, **44** (1920), 531; M. Ide, *Ibid.*, **46** (1921), 521.

6—A. D. Emmett and M. Stockholm, *J. Biol. Chem.*, **43** (1920), 287; G. de P. Sousa and E. V. McCollum, *Ibid.*, **44** (1920), 113; E. I. Fulmer, V. E. Nelson and F. F. Sherwood, *J. Am. Chem. Soc.*, **43** (1921), 186, 191; M. B. MacDonald and McCollum, *J. Biol. Chem.*, **45** (1921), 307; **46** (1921), 525; V. E. Nelson, E. I. Fulmer and R. Cessna, *Ibid.*, **46** (1921), 77; W. H. Eddy, H. L. Heft, H. C. Stevenson and R. Johnson, *Ibid.*, **47** (1921), 249; A. Harden and S. S. Zilva, *Biochem. J.*, **15** (1921), 438.

7—T. B. Osborne and L. B. Mendel, *J. Biol. Chem.*, **32** (1917), 369.

Vitamines from the Standpoint of Structural Chemistry[1]

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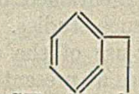
β-HYDROXYPYRIDINE

Previously published papers[2] have recorded the fact that β- as well as α-hydroxypyridine exists in two crystalline modifications. Dr. H. E. Merwin of the Geophysical Laboratory kindly examined a preparation and describes the two crystal forms as follows:

> The preparation contained crystals of two very different habits; crystals having one habit were lath-shaped with parallel extinction; γ, parallel to the long axis, equals or slightly exceeds 1.74; β; parallel to the intermediate axis, equals 1.600; and α, parallel to the short axis, is slightly greater than 1.575, but much less than 1.60. The crystals, therefore, are orthorhombic, with a small positive optic axial angle.
>
> Crystals having the other habit were equidimensional and possessed some well-formed faces, but the optical orientation could not be determined. They are optically positive, with moderate optic axial angle. α = or is slightly < 1.174, γ is slightly < 1.735.
>
> A few of the lath-shaped crystals were partly changed into aggregates of small crystals having α and γ like those of the equidimensional crystals. By warming the lath-shaped crystals on a slide somewhat below 100° this transformation in the solid state could be brought to completion within a few moments. Although the optical properties of the two kinds of crystals are so similar, there is no doubt that they are different forms.

β-Hydroxypyridine has heretofore been regarded as enolic, differing sharply from the α and γ isomers. This is not the case, for by titration with bromine[3] all three prove to be non-enolic in neutral solution, though largely enolic in sodium ethylate solution. The α and γ isomers have been shown to form both oxygen and nitrogen ethers,[4] but this was held to be impossible in the case of β-hydroxypyridine. As predicted in a previous paper,[5] β-hydroxypyridine forms a nitrogen-methyl ether which has the structure



thus establishing the complete parallelism of the β- with the α- and γ-hydroxypyridines. This nitrogen ether of β-hydroxypyridine is prepared from methyl iodide addition product[6] by shaking in aqueous solution with silver oxide. After filtration from silver iodide the solution is saturated with potassium carbonate. The supernatant oil which separates is dried over anhydrous potassium carbonate and distilled *in vacuo* (b. p. 300° at 2 mm.). The viscous oil is miscible with water in all proportions; nonvolatile with steam; reduces permanganate instantaneously and gives a white, crystalline precipitate with mercuric chloride; when decomposed in aqueous solution with sodium amalgam it yields copious amounts of primary amine, as shown by mercuric bromide. In all respects it resembles the α and γ nitrogen-methyl ethers and not the oxygen ethers. Analysis by Kjeldahl-Gunning-Arnold method gave 12.68 per cent nitrogen (calculated 12.85 per cent).

FEEDING EXPERIMENTS

Although the foregoing constitutes a definite contribution to the chemistry of the hydroxypyridines, no such decisive answer is possible as to their resemblance to vitamine B. Harden and Zilva[1] have failed to confirm the writer's findings as to the physiological action of α-hydroxypyridine. Their statements are not altogether convincing that the active form was actually administered or that the birds were well chosen for experiment. However, it must be conceded that the positive evidence of antineuritic action is equally unconvincing, inasmuch as no prophylaxis has been obtained with the substance. A protective feeding experiment is of vastly more value than numerous curative tests and such evidence must be forthcoming if it is to be beyond dispute.

Curative tests were made with a variety of substances and the results of some of them are recorded below.

SUBSTANCE	BIRDS TREATED	DOSE IN MG.	RESULT
Anthranil	5	1	Evidence of toxicity
Benzo-orthoxazinone	8	2–5	No improvement
β-Hydroxypyridine (mixture of 2 forms)	10	2	6 partly relieved 4 unaffected
β-Methylpyridone	5	2	4 substantially improved
Picolinic acid methylchloride	5	2–5	No effect

Protective feeding experiments have been made with a large variety of synthetic substances, including in addition to those used for curative tests the following: vicine, divicine, 6-oxypyrimidine, trimethyluracil, amino-trimethyluracil, dialuric acid, tetramethyl uric acid, methoxy caffeine, 1, 3, 7-trimethyl uric acid, isocytosine, and 4-phenylisocytosine. Only trimethyluracil and 4-phenylisocytosine gave any suggestion of protective effect.

4-PHENYLISOCYTOSINE

The writer's experience with 4-phenylisocytosine is as follows:

Following the directions of Johnson and Hill,[2] an attempt was made to prepare the four modifications described by them. Preparations were obtained which appeared to agree fairly well with three of the four isomers described by Johnson and Hill, but at no time was the fourth and most unstable form discovered. Its existence is by no means disputed, as experience with the various forms clearly indicated that apparently trivial modifications of method were sufficient to alter the result. The problem appeared baffling in the extreme. For example, β and γ forms, having the same melting point and identical crystallographic and optical properties as far as they could be measured, still differed from one another in that the β was approximately ten times as soluble in alcohol as the γ form. It was found impossible precisely to correlate crystal form with method of preparation, much less with physiological action.

A test was made by daily administration by mouth of 5 mg. of freshly prepared 4-phenylisocytosine to eight pigeons fed on a white rice diet. Four birds received preparation B and four preparation D, corresponding in appearance to Johnson's and Hill's β and δ forms. The birds were picked at random from the same group and the experiments were carried out simultaneously and side by side. All four birds given preparation B lost weight less rapidly than any of the four receiving preparation D. The result is precisely what would be expected if preparation B had contained a small amount of an antineuritic so unstable that it passed out of existence in the course of a few days. An experiment with the two identical preparations indicated no physiological difference two months later.

Whether this result or any of the physiological results so far obtained with synthetic substances has any real significance must be left to the reader's judgment. However,

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[1] The work here recorded was largely done at the Bureau of Chemistry. It was interrupted by the war and as no early opportunity to resume it can be foreseen the series of papers is closed with this record of some of the incomplete work which seemed most likely to be useful.

[2] R. R. Williams, *J. Biol. Chem.*, **25** (1916), 437; **29** (1917), 495.

[3] K. H. Meyer, *Ann.*, **380** (1911), 212.

[4] H. v. Pechmann and O. Baltzer, *Ber.*, **24** (1891), 3144.

[5] R. R. Williams, *J. Biol. Chem.*, **29** (1917), 495.

[6] Fischer and Renouf, *Ber.*, **17** (1884), 763, 1896.

[1] *Biochem. J.*, **11** (1917), 172.

[2] *J. Am. Chem. Soc.*, **36** (1914), 1201.

the solubilities, chemical reactions, and natural occurrence of vitamine B, so far as known, agree very closely with the pyrimidine bases, a class of substances known to be capable of a very delicate desmotropism. In view of these facts any suggestion of physiological activity in synthetic preparations of this group or its allies ought not to be lightly dismissed. The writer believes that vitamine B eventually will be found to be a cyclic nitrogen compound with an oxygen substitution in the ring and capable of existence in a betaine configuration. If the work on synthetics offers any useful suggestions as to manipulation in the isolation or identification of the vitamine from natural sources it will have served an adequate purpose.

Vitamines from the Standpoint of Physical Chemistry

By Victor K. LaMer

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To cover the subject of vitamines in detail from the standpoint of physical chemistry would require more time than has been allotted and for that reason the discussion will be limited to an outline of the subject, dwelling in detail only upon the more important phases. For the same reason the assumption is made that we have a quantitative method for measuring the vitamines in question, a method in which we know approximately at least the errors with which our measurements are burdened.

Granted that we have such a method, it then becomes feasible to interpret the data in the light of physical chemistry. This procedure promises results of practical value to the manufacturer of food products, who desires information in regulating his process so that he may obtain the maximum preservation of vitamines consistent with the other requirements of the process, and in addition it furnishes data of theoretical value which should aid us in establishing what the chemical structure of the vitamine may be and may not be.

The courses which these investigations have taken may be outlined as follows:

1—Studies on solubilities in different media.

2—Studies on the adsorption of vitamines under varying conditions.

3—Studies on the size of the particles which carry the vitamine activity, or more specifically studies on ultrafiltration.

4—Studies on the stability of the material under conditions in which time, temperature, hydrogen-ion concentration, radiant energy, and oxidizing agents are the independent variables.

For the most part studies made with these objects in view have appeared in the form of short, disconnected communications, from which it is difficult to interpret the results obtained because of variations in technique, but more often because some one of the variables just mentioned has not been controlled.

Solubility Studies

That the science is urgently in need of more uniform and quantitative measurements becomes apparent when we discuss solubility. The early studies on solubility led to the distinction in the vitamines; namely, A, B, and C. Later and more exacting studies have shown that this is but a rough method of classification and that the solubilities given refer only to the more characteristic solubility. The fat-soluble vitamine A in skim milk is a case in point. Some workers have tacitly considered that diets containing skim milk were free from vitamine A, since this vitamine is soluble in fat solvents. Experiments by McCollum, and later by Sherman, MacLeod and Kramer,[1] have shown that this assumption is false and that the amount of vitamine A in skim milk is roughly equal to that contained in the fat layer. When this result is interpreted in the light of the distribution law (since equilibrium exists between the phases) it will be seen that the ratio of the solubility of the vitamine in the oily phase and the aqueous is about 30 to 1. It is very likely that further studies would reveal a similar state of affairs for the other vitamines. For instance, Meyers and Voegtlin[1] have recently reported water-soluble B to be somewhat soluble in fat oil.

Adsorption Studies

Adsorption studies have been confined almost entirely to the type of experiments of Harden and Zilva,[2] who showed that the B vitamine was adsorbed by fuller's earth and dialyzed iron, while the C vitamine was not appreciably affected under the conditions of their technic. The authors rightly point out that the completeness of the adsorption is especially sensitive to changes such as H-ion concentration, so that it is necessary in reporting experiments of this type that all conditions be expressly stated. The claim of Ellis, Steenbock and Hart[3] that blood charcoal removes a measurable amount of the C vitamine from orange juice shows that the separation of B and C by this means is not quantitative.

Studies on Ultrafiltration

The same investigators have studied the effects of ultrafiltration and conclude that there is likewise a partial retention of vitamine C when Chamberland candles are used. It is well to emphasize that the nature of the pores and the character of the filtering material are important factors in such procedures. The recent work on colloids indicates more and more that the process of ultrafiltration, although it may give a crude measure of the size of particles, is far from being a simple case of mechanical separation and that instead the relative chemical nature of the material and the filter bag have much to do with the process.

Studies on Stability

Investigations upon the stability of the vitamines has received considerably more attention than have any of the types of investigation just mentioned, due very largely to the more practical aspects of such studies.

Strictly speaking,[4] the use of the term stability should not be applied to vitamines at present because this term refers solely to the effect of energy, usually in the form of heat, upon a substance, while the latter is carefully isolated from all other substances. The effects of the other components of the environment should be referred to as separate chemical properties. It is obvious then that we can speak of the stability of the vitamines only when we are careful to define the conditions under which the experiments are carried out.

Two years ago the writer, in conjunction with Professor H. C. Sherman and Miss H. L. Campbell of the Laboratory of Food Chemistry at Columbia, began research upon the stability of the antiscorbutic vitamine.

At that time it appeared from the work of Holst and Frohlich,[5] Delf,[6] and Hess,[7] that the destruction of the antiscorbutic vitamine could be expressed as some function of the temperature, the time of heating, storage, and the acidity. Since then it has become very evident that we must consider still other factors, such as the oxidation and reduction potential of the solvent medium, and perhaps the effects of radiant energy. It is the purpose of this paper to show as far as possible how these factors are related to one another.

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[1] *Proc. Soc. Exptl. Biol. Med.*, **18** (1920), 41.

[1] *J. Biol. Chem.*, **42** (1920), 199.

[2] *Biochem. J.*, **12** (1918), 93.

[3] *J. Biol. Chem.*, **46** (1921), 367.

[4] Alexander Smith, "Inorganic Chemistry" (new edition), p. 149.

[5] *Z. Hyg. Infectionskrankh.*, **72** (1912), 1.

[6] *Biochem. J.*, **12** (1920), 416.

[7] Hess and Unger, *J. Biol. Chem.*, **48** (1918), 297.

RELATION OF TIME OF HEATING TO TEMPERATURE

It was felt that the relative importance of the time of heating to the temperature of heating was the most important relation of all and accordingly the first experiments were made with the object of determining the functional relationship which existed between them. Comparisons were made of the quantities of antiscorbutic vitamines, given in the form of filtered canned tomato juice, that were necessary to protect guinea pigs against varying degrees of scurvy, when the tomato juice had been heated from 1 to 4 hrs. at 60°, 80°, and 100° C. From the data obtained it is easy to calculate the per cent destruction for each animal, the average of the results of four or more animals being accurate to ± 5 per cent. Inasmuch as the results of these investigations are being published in detail elsewhere, reference will be made here to only the more important conclusions.[1]

In the first place, the data show that the destruction of the antiscorbutic vitamine is of the nature of a chemical reaction in which the velocity is accelerated by increase of temperature. The velocity of the destruction reaction decreases with the progress of time in greater degree than does a reaction of the first order. Two explanations exist. Either the reaction is of a higher order, or another variable parameter is complicating the reaction under long-continued heating (4 hrs.). This phenomenon of flattened reaction velocity curves is not an uncommon one in reactions involving a complicated substrate such as we have in the hydrolysis of protein by pepsin. It has been found that the per cent destroyed at 60°, 80°, and 100° C. can be represented by the empirical equation

$$X = K\sqrt[4]{t}.$$

When t is the time expressed in hours, the values of K become 0.26, 0.39, and 0.49 for the temperatures of 60°, 80°, and 100° C., respectively. X = per cent destruction of the vitamine.

These values for the velocity constants show that the temperature coefficient of the reaction is below that of most ordinary chemical reactions, which are doubled or trebled for a 10° rise in temperature. Q_{10} has the low value of 1.1_2 between 80° and 100° and the value 1.2_3 between 60° and 80° C. These data exclude the possibility that vitamine C is of a protein- or enzyme-like nature.

While discussing the destruction of vitamines at low temperatures, particular attention should be called to the fact that merely measuring the amounts of vitamine extracts fed does not in itself constitute a quantitative determination for it is obvious that if the experimental animal is given more than it needs, efficiency effects will not be observed and the result will not be an accurate measure of the amount of vitamine given. It is only when quantities at or below the minimal protective dose are used that we are justified in drawing conclusions regarding the extent of destructive agencies.

Chick and Hume[2] have previously discussed this point, but their criticism has not been heeded by many of our American workers. The most recent violation of this principle appeared in a paper by Dutcher, Harshaw and Hall,[3] where the conclusion is drawn that no destruction of antiscorbutic vitamine occurs when orange juice is heated for 1 hr. at 63° C., a statement in conflict with the data just given for tomato juice. The writers of the article reach this conclusion from experiments in which only one level of intake is studied. The experiments show that the protective effect of 3 cc. of heated orange juice is practically the same as that of 3 cc. of unheated juice, as would be expected, since the minimal protective dose of orange juice, as redetermined by Davey,[1] is 1.5 cc., a value which is in conformity with Delf's earlier experiments. From these figures it is plain that any destruction under 50 per cent would not be observed when 3 cc. was the smallest quantity fed, but if both the heated and the unheated orange juice had been fed at a level of 1.5 cc., the results would doubtless have indicated a destruction comparable to the 25 per cent destruction we have observed in tomato juice under very similar conditions.

ACIDITY—Our studies on the effect of heating at reduced H-ion concentrations show that this results in an increase in the velocity of destruction. Thus 50 per cent is destroyed at the natural acidity, pH 4.3; when the organic acids are somewhat less than half neutralized, or pH = 5.2, the destruction is 58 per cent; at complete neutralization, or pH = 8.3, the destruction is about 62 per cent, the time and temperature being 1 hr. and 100° C. Further it was shown that the destruction was increased when the material was not reacidified back to the original acidity after heating, as was done in all of the cases just mentioned. Thus when the material was left alkaline and stored at 10° C., and fed over a period of 5 days, the destruction amounted to as much as 95 per cent.

TABLE I

No. of Animals	pH	RESULT
		Oxygen bubbled through
4.	4.3	Complete destruction. Acute scurvy in all cases, the animals dying within 27 to 36 days
3	8.3	
		Hydrogen bubbled through
3	4.3	Some protection—life prolonged to 42 and 50 days. 4-cc. animal still living on the 50th day
3	8.3	Some protection—life prolonged to 31, 46 days. 4-cc. animal living at 50th day but very scorbutic
		Air expelled before heating
12	4.3	50 per cent destruction } Life prolonged to 90 days or over
5	8.3	62 per cent destruction

OXIDIZING AND REDUCING AGENTS—To test the effect of oxidizing agents, tomato juice was put into flasks fitted to reflux condensers to prevent evaporation, the flasks were immersed in a boiling water bath, and either oxygen or hydrogen was bubbled through the juice. Since the oxidizing potential of oxygen and the reducing potential of hydrogen vary with the H-ion concentration, the tomato juice was tested both in acid and slightly alkaline solution and the results compared with our previous experiments, in which the air was first expelled by the water vapor coming from the boiling solution and a cotton stopper introduced to prevent re-access of air during the heating period. The results of preliminary experiments upon 13 animals fed at the levels of 2, 3, and 4 cc. are given in Table I.

While it would not be wise to draw too definite conclusions from the number of animals used, the concordance in the results makes one feel safe in concluding that the velocity of the reaction under the oxidation potential furnished by a saturated solution of oxygen in both acid and weakly alkaline solution is sufficiently rapid to destroy the vitamine completely in 1 hr. at 100° C.

We are inclined to interpret the other results as indicating that vitamine C is susceptible to a pure heat destruction, which may be increased by the addition of oxidizing or reducing agents, since somewhat greater destruction occurred when hydrogen was bubbled through when compared to the cases where no gas was used.

This interpretation makes it entirely possible that the heat destruction of vitamine C is of the nature of an intramolecular oxidation and reduction, such as occurs when aldehydes or sugars are heated, especially in alkaline solution (*i. e.*, Cannizzaro reaction), and the addition of external oxidizing or reducing agents simply serves to carry the

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[1] LaMer, Campbell and Sherman, *Proc. Soc. Exptl. Biol. Med.*, **18** (1921), 122; *J. Am. Chem. Soc.* [in press].

[2] *J. Biol. Chem.*, **39** (1919), 203.

[3] *Ibid.*, **47** (1921), 483.

[1] *Biochem. J.*, **13** (1921), 83.

equilibrium point of the reaction more in one direction or the other, thus increasing the velocity.

It is our intention to continue this study on the destruction of vitamine under the influence of experimentally measured oxidation and reduction potentials as soon as conditions permit.

The Antiberiberi Vitamine

By Casimir Funk

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The antiberiberi or B vitamine is the most important and the most frequently studied of this class of substances. Its discovery was contingent, as is well known, on the elucidation of the etiology of beriberi, a far-eastern disease, due to continuous consumption of polished rice. This vitamine is more or less distributed throughout the whole animal and vegetable kingdom, but in the cereal grains it is located chiefly in the germ and in the peripheral layers and therefore easily lost during the cleaning process applied to the grain.

As regards the function of this substance in the body, we know only that in its absence from the food general cachexia develops, similar to a severe inanition, the whole picture originating, as it seems, in the involvement of the central nervous system. Among the more important pathological changes is the increase in size of the suprarenals, going hand in hand with an increased adrenaline output. This observation put forward by McCarrison applies for the time being only to avian beriberi and may be brought into relationship with the present writer's observation that an increased carbohydrate consumption hastens the onset of the disease, showing perhaps that B vitamine plays a role in the carbohydrate metabolism. Contrary to this, a higher protein supply diminishes the needs for this vitamine and acts as a vitamine saver.

The present paper will deal briefly with the chemistry of B vitamine. The chemical studies deal almost exclusively with rice-polishings and, particularly, yeast, and were started about ten years ago. In dealing with this phase of the subject, very serious experimental difficulties were encountered, owing to the fact that no precipitation or color reaction specific for B vitamine is known. This substance is present in the starting material in minute quantities (as far as our present evidence goes, there is no more than a fraction of a milligram in a pound of dried yeast) and has to be separated from a large amount of inactive material, which is only partly becoming chemically known to us. The first endeavors were therefore directed toward a separation of the active material by the simplest possible procedure. Limiting the steps to a minimum is very important for the final success, as the time taken for the operations is an important factor in obtaining the final fraction in an active state. This separation was effected first by an extraction with alcohol, then by precipitation with phosphotungstic acid, tannic acid being used for the same purpose by Suzuki. Later came the adsorption with fuller's earth, introduced by Seidell, then the alcohol precipitation method of Osborne and Wakeman, the precipitation with bismuth potassium iodide by Hofmeister, adsorption with norit by Eddy, and so on. Unfortunately none of these methods shows any specificity for B vitamine, and the fractions obtained are contaminated with a large quantity of inactive material. More promising was the method of fractionating the phosphotungstates obtained from yeast by means of acetone, the active fraction being insoluble in this solvent and representing roughly only 10 per cent of the total precipitate.

ISOLATION OF B VITAMINE

The isolation of B vitamine was attempted by a number of investigators. In 1911 to 1913, the writer was able, by precipitation of the decomposed phosphotungstates with sublimate, silver nitrate in acid and finally in alkaline solution, to obtain a series of crystalline substances, one of which proved to be nicotinic acid, and another which after recrystallization to a constant melting point still exhibited marked curative properties for beriberi pigeons. These substances were analyzed at that time and their formulas tentatively established, but it is still uncertain whether we were dealing with B vitamine or whether the substance was yet contaminated with adsorbed active material—this in spite of the repeated crystallization. Whatever may be the final outcome, we had in hand a new substance which is worthy of further study. The vitamine research has brought to light a series of new substances, present in the starting materials in very small amounts, among them nicotinic acid, aschamine, and a recently isolated reducing substance, glucathion, obtained by Hopkins. It is clear, therefore, that the above-described attempts did contribute materially, and will do so more in the future, toward increasing our knowledge of chemistry of the living cell. From all the known reactions for B vitamine the most promising for the present is the precipitation with silver in alkaline solution. By using this method we obtain this vitamine in concentrated form, together with other substances which are largely known to us chemically. Among the substances which are carried down in this fraction, we know already the pyrimidines, histidine, histamine, glucathion (peptide composed of glutaminic acid and cysteine), guanidine, carnosine, and nicotinic acid, and we possess therefore ways and means to effect a successful separation of some of the impurities.

By using the combination of his fuller's earth method with the writer's silver method, Seidell was able to obtain a silver fraction which represents a small part of the initial yeast material. As we were able to ascertain in collaboration with Mr. Levy, this fraction contains a large proportion of inactive impurities.

NOMENCLATURE

In concluding the part of this paper relating to attempts at isolation of the B vitamine, the author wishes to dwell a moment on the question of nomenclature. A former assistant, Dr. Drummond, recently suggested dropping the final "e" in the term vitamine. This suggestion did not come as the result of experimental evidence, but merely on theoretical grounds. This may seem a trifling matter, but the suggestion has found already a number of followers. The name vitamine was given in the first place not so much to indicate the amine nature of these substances as for euphonic reasons. We were anxious to choose a name which would "take" and would stimulate workers in this new direction—and it did take. The final "e" was given to indicate the nitrogenous nature of these substances, in which the writer thoroughly believes. After all, the present evidence tends to show that the vitamines act as bases as well as acids and such substances have the ending "e" in the English language. By dropping the "e" very little is changed, the amine still being pronounced. In the absence of experimental evidence against these views, there is little necessity to effect a change of nomenclature at this time. In connection with a possibility of an acidic nature of this substance, we have sometimes succeeded and sometimes failed to distil in vacuum the free ester of the substance which acts on yeast. The experimental difficulty here is in the effective separation of the nondistilling material, which accumulates and causes decomposition at higher temperatures, showing at the same time the complexity of our present vitamine fractions.

IS B VITAMINE A MIXTURE?

Another problem of great interest is whether the substance with which we hitherto have dealt as B vitamine is one or a mixture of substances. For some time, indications have been present in the literature showing that we are dealing here with a mixture. In particular, Abderhalden and Schaumann have contended that there is a substance which acts on the nervous system, another one which acts in maintaining weight. In this country Emmett advocated the view that the substance for rats is not the same as for pigeons and is still different from that which acts on yeast. These views are undoubtedly correct, to a great extent. Recently, in collaboration with Dr. Dubin we succeeded, by fractional adsorption with either fuller's earth or norit, in separating at least two substances in a fairly complete manner. This separation will enable us to study these two substances more closely and also to determine their respective value in animal nutrition. Another field which will be influenced by the above separation is the nature of the substance which is important in the metabolism of lower organisms. Recently, the so-called yeast method was introduced for the quantitative determination of B vitamine. The above separation shows clearly that we are dealing here with two substances at least, one which cures beriberi, and the other which acts on lower forms of life. This second substance we propose to call D vitamine. The yeast method, showing the relative content of extracts in vitamines of the B-type, can no longer be regarded as specific for antiberiberi vitamine. Yeast is favorably influenced by D vitamine and we have no doubt that we are dealing here not with an improvement of the medium, as some workers have contended, but with a specific substance; this presents a new field of investigation for the future. As regards bacteria, the problem is more complicated, as these microörganisms require at least two substances, one present in the blood, possibly connected with the blood pigment, and another substance of the nature of the above-described D vitamine. Here also our adsorption procedure offers a distinct advantage over the methods hitherto employed, as it eliminates a large proportion of the impurities from the start.

Lack of Chemical Knowledge

In the chemical work on B vitamine we are still struggling with a difficulty which lies in the way of progress and success. The present methods seem to injure the activity of the substance. This is undoubtedly due to our lack of knowledge of the chemical characteristics of these substances. It seems that in the case of B vitamine we are not dealing, as in the case of other vitamines, with the injurious effect of oxidation. There is something else to be looked for and it seems to the writer that so long as we do not possess a specific precipitation method or know how to stabilize this substance so that one would have the time to study its characteristics, no definite progress can be made. Unfortunately the vitamines, like the rare gases of the air, have so far shown exceedingly little affinity for the known reagents, most of which no doubt have been tried. For the present, therefore, we have to contend with the elimination of impurities; this necessitates slower procedure and we are handicapped by the imperfect chemical knowledge of the latter.

Views are often expressed as to the exaggerated importance assigned to the vitamines. There is no doubt that vitamines do not mean everything in nutrition. One cannot live without vitamines, but one cannot live with vitamines only. There are some who hold that the vitamines are only a fad in science, which will pass away as many other fashions have passed. This is not so; the vitamines are here to stay. Their chemical nature may be difficult to establish, but the price of the efforts will be well worth while. It will open up new viewpoints and bring new ideas. It is therefore a pity that only few organic chemists venture into this field, offering possibilities of new and unexpected developments. For the chemical study of the vitamines, vitamine B, or perhaps better still the above-mentioned vitamine D, offers the best opportunity on account of greater stability. We have to start with the study of the most stable vitamine. Knowing the chemical nature of one such substance, it may prove easier to arrive at the others.

Experiments on the Isolation of the Antineuritic Vitamine

By Atherton Seidell

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It is generally acknowledged in recent contributions to the subject that no trustworthy information concerning the chemical nature of any vitamine has, as yet, been obtained. On the other hand, the study of the functions of the several vitamines is progressing rapidly and is closely approaching quantitative exactness in some cases.

The failure to make substantial progress in the chemical isolation and identification of vitamines is due to the length of time required for, and the uncertainties of, the physiological tests available for controlling the fractionations, and more particularly to the readiness with which the characteristic vitamine activity disappears during the laboratory manipulations. In this respect it is a common experience to find that the product finally isolated is devoid of the characteristic physiological action of the original crude material. Some investigators consider it an axiom that the better the final product appears from the chemical standpoint, the worse it will be found when tested for its physiological activity.

It is probable that by far the greater number of the experiments which have been made on the isolation of vitamine are useful principally in showing how the problem cannot be solved and have, therefore, been withheld from publication. A considerable number of the present series are of this type and are omitted. Although those which are given do not furnish a solution to the problem of the true chemical nature of vitamine, they appear to supply another stepping stone toward this goal. A method is described by which a relatively stable silver precipitate, which undoubtedly possesses considerable vitamine activity, can be obtained. It is hoped either that the identity of the active constituent of this product can be established or that the pure vitamine itself may eventually be isolated from it.

The discovery of this new vitamine complex was briefly described in a preliminary paper[1] published several months ago. The reaction involved has since been studied in greater detail and much additional information obtained in regard to it. Briefly, it consists in subjecting a concentrated vitamine extract to successive precipitation with aqueous silver nitrate and ammoniacal silver nitrate. The latter precipitate has been found to contain by far the greater part of the vitamine originally present. Since it is probable that the method of preparing the aqueous vitamine extract used for the precipitation contributes largely to the success of the procedure, this will first be described.

Preparation of Concentrated Vitamine Extract from Brewer's Yeast

The fresh yeast, as obtained from the brewery, is allowed to autolyze and the thick liquid thus obtained is filtered. English fuller's earth[2] is added to the clear autolyzed filtrate in the proportion of 50 g. per liter and, after thorough shaking,

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[1] Atherton Seidell, "Preliminary Note on a Stable Silver Vitamine Compound Obtained from Brewer's Yeast," *Public Health Reports*, April 1, 1921, p. 665.

[2] The variety occurring at Surrey, England, and imported by Eimer and Amend.

removed by filtration, washed, and dried. This material, called for convenience "activated fuller's earth," is extracted by means of aqueous saturated barium hydroxide solution. The time of contact of the alkaline solution with the solid must be brief. One liter of barium hydroxide solution is used for each 100 g. of the activated solid and the clear liquid, which is separated from the well-shaken mixture, is acidified promptly with a slight excess of strong sulfuric acid. The excess of acid is neutralized by addition of powdered barium carbonate and the milky liquid is filtered. The resulting clear solution is then subjected to lead acetate precipitation and, after filtration, the lead is removed from the filtrate by means of hydrogen sulfide. This final dilute aqueous extract of vitamine is concentrated to a small volume by rapid vacuum distillation. The white amorphous material which separates toward the end is removed by filtration, and the final concentrated extract is reduced to a thick pasty semisolid condition by allowing it to stand several days in a vacuum desiccator.

SILVER NITRATE PRECIPITATION

Of the several factors which modify this reaction, little definite information has been obtained. Furthermore, it is probable that variations in the composition or condition of the vitamine extract exert an influence outweighing all others. Consequently, considerable variations in the appearances and yields of the several fractions may be encountered. In general it has been the custom to conduct the precipitation in relatively small volumes of solution. This was considered to reduce losses due to solubility or hydrolysis of the compounds.

The semisolid vitamine extract obtained from 300 g. of activated solid is usually dissolved in somewhat less than 50 cc. of water and the clear filtered solution precipitated in a centrifuge tube by the dropwise addition, with constant stirring, of a nearly saturated solution of silver nitrate. A curdy white precipitate forms around each drop and its accumulation may finally render the mixture nearly solid. On centrifuging, the supernatant clear liquid is tested for completeness of the precipitation, and when this point is reached the curdy solid is washed by stirring successively with about an equal volume of water, centrifuging, and decanting. During this time the precipitate gradually darkens and may become almost black. In the following pages the precipitate obtained by addition of silver nitrate is designated as (I).

The supernatant liquid and wash water, which give no further precipitate with aqueous silver nitrate, are then precipitated in an exactly similar manner with a concentrated ammoniacal silver nitrate solution. This latter is conveniently made by gradually adding strong ammonia to a concentrated silver nitrate solution until the black silver hydroxide, which at first separates, just redissolves. The curdy precipitate now obtained is similar in volume and appearance to that produced by addition of silver nitrate. It is washed by centrifugation and rapidly becomes dark in color. The precipitate obtained with ammoniacal silver nitrate is hereafter designated as (II).

With vitamine extract made from certain samples of "activated solid" which had become somewhat moldy, no ammoniacal silver precipitate (II) was obtained at this stage. In these cases it was found that precipitate (II) appeared first during the reprecipitation of (I), as will be described in the succeeding paragraphs.

The question as to whether the two precipitates, (I) and (II), should be dried by spreading on a porous plate after this and succeeding reprecipitations has not been settled. This has been done in some cases and in others not, but the effect, if any, on the final yield of active material has, so far, not been established by physiological tests.

Both (I) and (II) are decomposed by suspending in about 25 cc. of water and passing a rapid stream of hydrogen sulfide through each mixture until the conversion of the silver to sulfide appears complete. The silver sulfide is conveniently separated by centrifugation and the clear supernatant liquid filtered. After volatilization of the excess of hydrogen sulfide by slight warming and subjection to diminished pressure, the solutions are each subjected to reprecipitation with the silver nitrate and ammoniacal silver nitrate reagents exactly as done in the first place.

Fraction (I) now yields a precipitate with silver nitrate and the supernatant liquid from this furnishes a considerable amount of precipitate on addition of ammoniacal silver nitrate. This is later added to the main portion of precipitate (II).

The original fraction (II) gives only an insignificant amount of precipitate with silver nitrate and the product now obtained with ammoniacal silver nitrate turns dark much more slowly than during the previous precipitation. Furthermore, after the precipitation with ammoniacal silver nitrate is brought to completion, the supernatant liquid may yield a further amount of curdy precipitate by addition of silver nitrate. This is particularly true for the third precipitation and it therefore appears that for complete silver precipitation a narrow adjustment of the proportions of the two reagents is required. In some cases the second and subsequent precipitations of (II) have been made by alternate additions of silver nitrate and ammoniacal silver nitrate solution. The final clear supernatant liquid obtained by centrifugation is always tested with both reagents before being rejected.

Both (I) and (II) should be washed one or more times by stirring with water and centrifuging and then spread on porous plates to dry. During the drying the precipitates contract in volume and (I) always turns dark brown or black in color. In the case of (II) the darkening is usually not so pronounced. After a third precipitation and sometimes after the second, (II) retains its white color during the drying, but no sample of (I) has so far been found to retain its original white color after being dried on the porous plate.

The ammoniacal silver nitrate precipitate (II) obtained from the first silver nitrate precipitate (I) is mixed with that obtained by reprecipitation of the first ammoniacal silver nitrate precipitate (II). This mixture is suspended in water and treated with hydrogen sulfide as was previously done. The clear filtrate from the silver sulfide, when freed of the excess of hydrogen sulfide, is precipitated as previously described, and ordinarily constitutes the final pure antineuritic product which has previously been designated as "silver vitamine compound." The average quantity of the dry white product obtained from 300 g. of "activated solid" is 2.5 g.

CHEMICAL NATURE OF THE SILVER PRECIPITATES

PRECIPITATE (I)—It is well known that many compounds, particularly purines, give curdy, insoluble precipitates with silver nitrate both in acid and alkaline solution. In the present case it has been found that the two or more times reprecipitated silver nitrate fraction (I) is mainly, if not entirely, a silver compound of adenine. The identification of this purine was made by decomposing the precipitate suspended in water, with hydrogen sulfide, and slowly evaporating the filtrate from the silver sulfide, to crystallization. The crystals which separate respond to the phenolsulfonic acid test for nitrate and yield an insoluble picrate which corresponds in all its properties to adenine picrate. The melting indications of the latter are unchanged when mixed with an approximately equal amount of authentic adenine picrate. The percentage of nitric acid in the crystals, as estimated by colorimetric comparison of the products of the phenolsulfonic acid reaction, corresponds closely with that required for adenine nitrate. The yield of adenine nitrate obtained in this way from 300 g. of activated fuller's earth was, in several cases, found to be about 0.5 g.

Since no nitric acid was added in the above experiment, it is evident that the amount required to form the crystalline adenine nitrate must have been derived from the silver adenine precipitate. In order to obtain information on this point, and also on the silver content of the precipitate, four samples prepared from different lots of vitamine extract were analyzed, by ignition, for silver, and by the colorimetric phenolsulfonic acid method, for nitrate. The following results were obtained:

SAMPLE No.	Per cent Ag	Per cent HNO_3
1	46.84	12.0
2	42.89	17.4
3	46.87	15.8
4	41.15	21.0

Sample 1 was a composite lot of six dried silver nitrate precipitates obtained by various slight modifications of the general method.

Sample 2 was obtained by precipitating three times and drying thoroughly after each precipitation.

Sample 3 was likewise dried after each of the three precipitations. It was obtained from a vitamine extract prepared from a sample of activated fuller's earth less active, physiologically, than that used for the preceding precipitates.

Sample 4 was prepared by precipitation of the mother liquor from adenine nitrate crystals obtained from a solution prepared by decomposition of the initial silver nitrate precipitate (I) by means of hydrogen sulfide.

These results, therefore, represent a considerable range of variation in the preparation of the silver nitrate precipitate (I). The constant presence of nitrate or nitric acid in these well-dried samples is noteworthy.

The results for per cent of silver agree in general with the accepted formula, $C_5H_4N_5Ag$ (= 44.4 per cent Ag), for adenine silver, but when the presence of the nitrate is taken into consideration the agreement is not so good. The fact that the nitrate is retained so persistently by this precipitate (I) and by the ammoniacal silver nitrate precipitate (II), as will be shown later, is believed to be of significance in explaining previous failures to isolate active crystalline material.

PRECIPITATE (II)—Turning now to the characteristics of the ammoniacal silver nitrate precipitate (II), it is found that a part, or in some cases all of it, may accompany the silver nitrate fraction, during the first precipitation of the crude vitamine extract. When, however, it has been separated completely from the latter by reprecipitation, it then does not yield a precipitate with silver nitrate in absence of ammonia. Fraction (II) rapidly redissolves in excess of the ammoniacal reagent or of ammonia. Furthermore, its reprecipitation is usually not complete with ammoniacal silver nitrate alone. The addition of silver nitrate after the end-point with ammoniacal silver nitrate yields in these cases a further considerable quantity of precipitate. Thus an alkalinity represented by less ammonia than required for complete re-solution of ammonia-precipitated silver hydroxide is necessary for maximum precipitation of (II). These characteristic differences between (I) and (II) show conclusively that some other compound than adenine is responsible for the properties of fraction (II), which the physiological tests, as previously reported, have shown to possess considerable antineuritic activity.

In regard to the composition of fraction (II), as shown by analysis, it is found that the silver content varies over a wide range but is much higher than found for the silver nitrate fraction (I). The content of nitrate (nitric acid) is, however, much lower. Results for seven samples are as follows:

SAMPLE No.	Per cent Ag	Per cent HNO_3
1	55.0	10.8
2	55.6	5.1
3	57.5	5.4
4	62.0	Not det.
5	49.4	6.7
6	46.0	4.3
7	51.5	6.8

Sample 1 was prepared by three precipitations, drying each thoroughly on a porous plate before proceeding to the next.

Sample 2 was precipitated from the mother liquor of the crystals obtained from Sample 1, by decomposition in the usual manner with hydrogen sulfide and slow evaporation of the filtrate from the silver sulfide. The yield from 3.68 g. of No. 1 was 0.46 g. of crystals, 0.57 g. of precipitate with ammoniacal silver nitrate, and 0.6 g. with silver nitrate. There was, consequently, considerable unaccounted loss.

Sample 3 was twice precipitated and dried on a porous plate after each precipitation.

Sample 4 was not dried on a porous plate after each precipitation, but was washed three or more times by stirring with somewhat more than an equal volume of water, centrifuging, and decanting the wash water.

Sample 5 was dried on a porous plate after each of three precipitations.

Sample 6 was obtained from the first silver nitrate precipitate and was not reprecipitated.

Sample 7 was prepared from "activated solid" which had begun to show evidences of molding and was of reduced vitamine activity. An exceptionally large amount of fraction (I) was obtained and none of fraction (II) at the first precipitation. The aqueous solution prepared by hydrogen sulfide decomposition of (I) was first subjected to crystallization and from the mother liquor, the present sample was obtained by the usual silver nitrate and ammoniacal silver nitrate precipitation.

As before, the silver was determined by ignition and the nitric acid by the phenolsulfonic acid colorimetric procedure. In this case, however, it was necessary to remove the silver from the alkaline solution before making the color comparisons. This was done by acidifying with hydrochloric acid, filtering, and restoring the color by adding excess of alkali.

A noteworthy point, in connection with these results, is that the percentage of silver was highest in Sample 4, in the preparation of which more washing was employed than in any other case. This would indicate that the precipitate is hydrolytically decomposed, with excessive removal of the more soluble organic constituent of the complex. This, taken in connection with the solubility of the precipitate in excess of ammonia, emphasizes strikingly the practical impossibility of controlling the conditions in a manner which might insure a product of constant composition.

Another point of interest is the constant presence of nitrate (or of nitric acid), even in samples which were repeatedly dried on a porous plate and by vacuum desiccation. It is regretted that Sample 4 was exhausted before the nitric acid determinations were made.

Experiments made with the object of separating in a pure condition the active compound united with silver in fraction (II) usually result as follows: The well-dried sample is suspended in water and hydrogen sulfide passed in to convert the silver to sulfide. The aqueous filtrate from this, when evaporated slowly, first yields a small amount of crystalline crusts which adhere to the sides of the dish above the surface of the evaporating liquid. By decanting at the proper time gradual crystallization may occur and large, well-formed, prismatic crystals slowly develop throughout the concentrated liquid. The exact conditions for the gradual crystallization are, however, difficult to realize, and usually the volume of liquid simply continues to diminish until it is a thick viscous mass. When it reaches this condition of supersaturation, stirring with a glass rod causes immediate crystallization, and the sirupy liquid is quickly transformed to a solid mass of minute crystals. The removal of a certain amount of the adhering mother liquor from this mass can be effected by spreading on a porous plate.

In one case in which the large crystals were obtained they were found to darken gradually and to melt with effervescence at about 205°. In the case of all the other samples, which were obtained by crystallization induced in a supersaturated solution and were dried on a porous plate, the melting point was found to be at approximately 178°.

The yield of the 205° crystals from 300 g. of "activated solid" was in the one case 0.46 g. The yields of the less pure 178° product obtained from the same amount of "activated solid" were 0.8, 1.02, 1.14, and 1.12 g., respectively. The 1.02 g. sample contained approximately 40 per cent of HNO_3, determined by the phenolsulfonic acid colorimetric method.

If the 178° crystals are dissolved in very little water and absolute alcohol is added, a point will be reached at which a white cloud separates. This gradually changes to minute needle-like crystals. The addition of ether appears to increase the yield of these fine crystals. When they are filtered off, washed with ether and dried, they melt quite sharply with only slight darkening and gas evolution at 214°.

These crystals dissolve instantaneously in water, and the solution gives no precipitate with aqueous silver nitrate alone but does when ammonia is added. Ammoniacal silver nitrate naturally gives an immediate curdy precipitate which redissolves in excess of the reagent or of ammonia. The aqueous solution of the crystals gives no precipitate with picric acid or sodium picrate. Likewise, no separation of an insoluble compound occurs upon addition of iodine solution or of mercuric chloride. A white precipitate is, however, obtained with phosphotungstic acid. An approximate determination of the nitric acid content of the crystals by the phenolsulfonic acid method gave 31.3 per cent.

From a consideration of the above properties, it appeared probable that the compound might be histidine nitrate. A positive test obtained on applying Pauly's reaction with *p*-diazobenzenesulfonate strengthened this view. The only nitrate of histidine mentioned in Abderhalden's "Biochemisches Handlexikon" is the dinitrate which contains 44.8 per cent HNO_3 and melts at 149° to 152°. Mononitrate would contain 28.9 per cent HNO_3. It was, therefore, decided to attempt to prepare histidine mononitrate and determine its melting point alone and when mixed with the present sample.

The mononitrate was prepared by mixing the calculated quantities of histidine and nitric acid and crystallizing from ether-alcohol. The resulting crystals melted at 232°. A mixture of about equal parts of this sample and the crystalline nitrate obtained from the ammoniacal silver nitrate fraction (II) began to soften below 150°, and complete liquefaction, with considerable effervescence, occurred some time before the temperature reached 200°. This appears to be satisfactory evidence that the unknown nitrate from fraction (II) cannot be histidine mononitrate.

Of the other known compounds which respond to the reaction with *p*-diazobenzenesulfonate, histamine (β-iminazolyl-ethylamine) corresponds very closely with histidine in many of the reactions. Tests were, therefore, sought to differentiate between the present sample and histamine. Of these the indications of the biuret reaction were inconclusive since an undoubted positive test could not be obtained with either a sample of authentic histidine or the unknown nitrate from the silver fraction (II).

It is stated that the dipicrate of histamine is very sparingly soluble in water. All attempts to obtain an insoluble precipitate on adding sodium picrate to a solution of the unknown nitrate were unsuccessful. It, therefore, appears improbable that the present crystals are a salt of histamine, but a final decision on this point requires further evidence.

In this connection, it should be mentioned that Dr. M. X. Sullivan of this laboratory states that he was able to identify histamine in vitamine fractions obtained by him several years ago, but he has, so far, not published his experiments.

Of the other compounds which respond to the Pauly *p*-diazobenzenesulfonate reaction, and correspond very closely in other respects with the nitrate here described, carnosine nitrate is stated to melt at 211° to 212°. Its content of nitric acid, however, as calculated from the accepted formula, is 21.8 per cent, therefore making it improbable that the present compound, containing 31.3 per cent HNO_3, can be carnosine nitrate.

PHYSIOLOGICAL TESTS

Physiological tests of the various samples described in the previous pages were made by administering measured doses at regular intervals to pigeons given polished rice as their sole food. Under these conditions the vitamine content of the sample can be roughly estimated from the changes in weight of the pigeon, as compared with control pigeons receiving no added vitamine. In some instances curative tests were also made. In these cases the pigeons, receiving an insufficient amount or no vitamine, are allowed to proceed to initial but well-marked polyneuritic condition and then given doses of the sample in question. A prompt alleviation of the typical symptoms, followed by protection from recurrence of polyneuritis for several weeks, was taken as evidence of the curative and at least partly protective properties of the sample.

In general, control pigeons begin to lose weight promptly on a polished rice diet and decline to about 60 per cent of their original weight and develop typical polyneuritis within about 20 days. Occasionally, however, birds may decline at a slower rate and finally die after 40 to 60 days without showing any well-marked paralysis. A considerably larger number of such birds than ordinarily met have rendered some of the present results less definite than might be desired.

Previous experiments with the silver nitrate precipitate (I) had shown it to be inactive. In regard to the recent results with the ammoniacal silver nitrate precipitate (II), it was found that in all cases prompt and complete cures of polyneuritis resulted from doses of 0.004 g. of sample, and repeated similar doses, on alternate days, prevented recurrence of polyneuritic symptoms for as long as the experiment was continued, which was usually three or more weeks. In no case, however, did a marked increase in weight occur. Furthermore, administration on alternate days of 0.004 to 0.008 g. doses of the thoroughly dried precipitate (II), did not prevent loss in weight of normal birds, as is found to be the case when adequate doses of "activated solid" or of crude vitamine extract are given. In these cases the rate of loss was at first approximately the same as that of control birds, but after a few weeks the curves began to flatten and a distinct advantage, resulting from the samples, was noticeable. The fact that polyneuritic birds are so greatly benefited by the silver compound and that normal birds apparently utilize it very slightly is difficult to explain.

The experiments made with the various fractions obtained from the silver precipitates showed that none was the equal of the silver precipitate (II) in relieving polyneuritis and preventing its recurrence.

An explanation of the repeated failures to secure active material from the silver complex may be found in the constant presence of nitric acid in this product and the consequent presence of this acid in every solution from which crystals were obtained. The suggestion for this explanation was obtained from one of the early experiments in which a crystalline nitrate was intentionally prepared from the ammoniacal silver precipitate and, when subjected to tests on pigeons, found to be entirely devoid of any curative or protective properties. The fact that all of the other crystalline products were nitrates was not ascertained until after completion of the physiological tests.

SUMMARY

Of the insoluble compounds obtained from concentrated vitamine extracts by successive precipitation with silver nitrate and ammoniacal silver nitrate, the first was found to consist principally of adenine silver and the second of a silver compound of a base closely related to histidine. Both precipitates tenaciously retain nitrate or nitric acid and this

remains in the solution after removal of the silver, with the result that the crystals, which are obtained on slow evaporation, are in both cases nitrates.

Feeding tests of the several crystalline compounds on pigeons showed that they retain very little, if any, of the antineuritic properties of the ammoniacal silver precipitate. It is possible that the loss of activity may result from the constant presence of nitric acid in the solutions from which the crystals are obtained.

The Antiscorbutic Vitamine

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Far less is known of the antiscorbutic vitamine[1] than of the antineuritic vitamine. We know that the antiscorbutic vitamine is water-soluble; indeed, it has been called the water-soluble C vitamine. It is also soluble in alcohol and in acetone. It is not adsorbed by the fuller's earth method introduced by Dr. Seidell; in fact, from a mixture containing both water-soluble B and C vitamines it can be separated by this means.

Little more is known from a purely chemical point of view. But that does not imply that considerable progress has not been made in the past few years in regard to this vitamine. Indeed, since the publication of the report of the British Research Committee, only three years ago, views have altered essentially in this regard. It was previously supposed, and brought forth in 1918 in this report, that this vitamine is destroyed by drying, by aging, by the canning process, and by heating. That had long since been the accepted view in regard to the factors which lead to the destruction of the antiscorbutic vitamine and bring about the development of scurvy. Recently our ideas in this respect have undergone important modifications. Without going into detail in regard to drying, it may be stated that experiments of Dr. Unger and the writer,[2] substantiated by others, have clearly shown that although most substances lose the vitamine in the course of drying, desiccation does not necessarily destroy this vitamine. For instance, milk may be dried to a powder and nevertheless retain the major part of its vitamine. This dried milk may even be aged and still retain this vitamine. *It may be canned and aged and dried and still retain its antiscorbutic vitamine* and be able to cure infantile scurvy. In the course of the desiccating process it is subjected to about 240° F., so that we may add, it also may be heated and nevertheless remain antiscorbutic. It is evident that there must be some other factor or factors involved in its destruction.

Reference should be made in passing to the importance of the reaction of the medium to the stability of this vitamine. It is known to most of you that if an antiscorbutic food is acid, it is much less apt to undergo destruction. For instance, this is the main reason why orange juice can retain its highly antiscorbutic potency in spite of having been boiled. It explains why the tomato is a very efficient antiscorbutic, even after it has been heated, canned, and allowed to age. In our experience tomatoes canned a year were found to have retained their full antiscorbutic value.

Clearly there must be some further explanation for the instability of the antiscorbutic vitamine; heat, to which its destruction has almost universally been attributed, cannot be the sole or even the preëminent factor. The clinical reports of experienced physicians also lead to this conclusion. For instance, children's specialists in France have reported that they have fed thousands of babies on hundreds of thousands of bottles of sterilized milk in the course of years, milk that had been heated to the boiling point and over and that throughout this long period they have never encountered a case of scurvy. Surely, such extensive reports covering a period of years cannot be passed over lightly.

Effect of Oxidation on Destruction of Vitamine

Some experiments carried out by the writer in conjunction with Dr. Unger showed that there is another factor, perhaps a more important factor than those mentioned, which leads to the destruction of this vitamine, namely, *oxidation.*[1] This action can be demonstrated in a very simple way. For instance, if a liter of milk is treated with a very small amount of hydrogen peroxide (4 cc. of a normal solution) and allowed to stand over night in an incubator at blood heat, the antiscorbutic vitamine is almost entirely destroyed. This is tested by the biological method; 80 cc. of milk per day per capita are fed to a series of guinea pigs. It is found that all these guinea pigs develop scurvy, whereas control guinea pigs receiving the same amount of milk to which peroxide has not been added remain free from signs or symptoms. Furthermore, the guinea pigs which develop scurvy on this oxygenated milk rapidly lose all symptoms of this disorder when a few cubic centimeters of orange juice are added to the dietary. In other words, the small amount of peroxide thoroughly destroyed the antiscorbutic content of the milk, destroyed it to the same extent as heating milk to 100° C. for an hour. The authors showed also that if orange juice is subjected to a stream of oxygen its antiscorbutic potency is likewise diminished, and that the same is true of milk. This destructive effect of oxidation has been substantiated by experiments carried out by Dutcher[2] in this country and by Zilva at the Lister Institute in London.[3] That antiscorbutic vitamine is sensitive to oxidation is of importance from a theoretical as well as from an industrial point of view. It explains, for instance, why some dried milk possesses the antiscorbutic property, whereas other dried milk is markedly lacking in this factor.

When we stated some years ago that experiments showed that dried milk may have antiscorbutic value, our conclusions met with skepticism. It is now recognized that the nature of the product depends upon the process of drying. If, in the course of drying, milk is subjected to oxygenation, as it is in the spraying process, it loses much or most of its antiscorbutic vitamine, whereas if it is dried on a drum and its particles not subjected to the air, it is found to retain the greater part of this vitamine. Condensed milk retains considerable of this factor, owing to the fact that the condensation process is conducted with very little access of air. This new conception of the role of oxidation harmonizes many views which heretofore appeared discordant. It explains how the French physicians were probably quite correct when they reported encountering practically no scurvy in the course of feeding sterilized milk to babies; we had paid no attention to the fact that the milk which they fed had been heated in and kept in hermetically sealed bottles.

This probably is the more precise explanation of what we have called "aging," a term which is descriptive but hardly scientific. The aging which destroys the antiscorbutic vitamine is oxygenation.

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[1] For fuller information on this subject reference may be made to the following papers by the author: "The Role of Antiscorbutics in Our Dietary," *J. Am. Med. Assoc.*, **71** (1918), 941; "Newer Aspects of Some Nutritional Disorders," *Ibid.*, **76** (1921), 693.

[2] "The Scurvy of the Guinea Pigs. III—The Effect of Age, Heat, and Reaction of Antiscorbutic Foods," *J. Biol. Chem.*, **38** (1919), 293.

[1] "The Destructive Effect of Oxidation on Antiscorbutic Vitamine," *Proc. Soc. Exptl. Biol. Med.*, **18** (1921), 143.

[2] R. A. Dutcher, H. M. Harshaw and J. S. Hall, "Effect of Heat and Oxidation on Antiscorbutic Vitamine," *J. Biol. Chem.*, **47** (1921), 483.

[3] "The Influence of Aeration on the Stability of the Antiscorbutic Factor," *Lancet*, **1921** [I], 478.

CATALYSIS

Another factor in the destruction of antiscorbutic vitamine is catalysis. Its effect may be illustrated by citing the following experiment. If milk is pasteurized (145° F. for 0.5 hr.), heating half of it in a glass vessel, and the other half in a copper vessel for the same length of time, the milk heated in the copper vessel will be found to have lost considerable of its antiscorbutic vitamine. On feeding 80 cc. per capita of these two lots of milk to a series of guinea pigs, the animals receiving the milk pasteurized in the copper vessel will develop scurvy, whereas those receiving the milk which had been heated in the glass vessel will thrive and not develop this disorder. That the signs and symptoms are truly those of scurvy is proved by their prompt disappearance—in spite of continuing the same milk—if a few cubic centimeters of orange juice are given in addition. The milk heated in the copper vessel contained but three or four parts of copper per million—a very small amount.

This experiment has a practical application for, as is well known, milk in the process of pasteurization passes through copper pipes; it is true that these are lined, but the lining frequently becomes defective after a short period. Lined copper vessels are commonly used in the course of condensing and drying milk. It is, therefore, not astonishing that copper is found very frequently in small amounts of milk. In a British medical report, it was found eleven times in eighty-seven samples. It is impossible to state how important a factor catalysis is. But whatever may prove to be the scope of its application, an experiment of this nature shows the little suspected factors which may be introduced and which must be taken into consideration in relation to the destruction of this most delicate vitamine, and warns us that in the handling of food products containing vitamines we must consider the influence of every new industrial process.

Quite apart from the question of the destruction of the vitamines, the last few years have demonstrated that we should not consider foodstuffs as entities from the standpoint of their vitamine content. A food may be rich or poor in this factor according to attendant circumstances. For instance, carrots cannot be classed as containing a definite amount of antiscorbutic vitamine; if they are fresh they will contain much more than if they are old, or, again, if they have been plucked young, they will have far more than if they were tough and old. We must avoid cataloguing foods too rigidly. It is probably of aid to arrange them in categories and to assign them definite potencies, but we must remember that such a list possesses merely comparative and approximate value.

ORIGINAL PAPERS

NOTICE TO AUTHORS: All drawings should be made with India ink, preferably on tracing cloth. If coördinate paper is used, blue must be chosen, as all other colors blur on reduction. The larger squares, curves, etc., which will show in the finished cut, are to be inked in.

Blue prints and photostats are not suitable for reproduction.

Lettering should be even, and large enough to reproduce well when the drawing is reduced to the width of a single column of THIS JOURNAL, or less frequently to double column width.

Authors are requested to follow the SOCIETY'S spellings on drawings, *e. g.*, sulfur, per cent, gage, etc.

Some Factors Affecting the Stability and Inversion of Oil-Water Emulsions[1,2]

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SCOPE OF INVESTIGATION

This work covers some preliminary results obtained in the course of a fundamental investigation of the properties and behavior of mineral oil-water emulsions. Exact information regarding the properties of commercial emulsions is difficult to obtain and classify accurately on account of the complexity of the factors involved. It is felt that by obtaining more complete information regarding the general principles which govern the behavior of emulsions in simple systems and then applying the information to a systematic study of more complicated emulsions, greater progress may be made than by starting at once with the study of a few complex emulsions which happen to be of commercial importance.

Much, though not all, of the work thus far undertaken has dealt with the inversion point of oil-water emulsions. By definition the inversion point is that point where there is a change from an oil-in-water type of emulsion to a water-in-oil, or *vice versa*. This evidently marks a region of instability, and hence is of practical importance from the standpoint of breaking emulsions.

In general the work has been divided into three phases: (1) an investigation of the factors affecting the inversion point in the case of emulsions with water of a highly purified oil like Nujol; (2) in emulsions containing Nujol to which substances which are known to be present in commercial oils have been added; and (3) in the case of emulsions of different commercial oils. From such investigations, it is hoped that much fundamental information may be obtained which should be of assistance in solving the difficult problems involved in breaking commercial emulsions.

SOME GENERAL PROPERTIES OF OIL-WATER EMULSIONS

Although there is much information in the literature regarding emulsions, correlation of the results of various investigations is difficult on account of the difference in the nature of the materials used, the method of studying the emulsions, and the complexity of the factors involved.

From a consideration of the literature and from scattered information obtained from various oil companies, an attempt has been made in the chart in Fig. 1 to enumerate some fundamental properties of importance in considering the stability of commercial emulsions. Referring to this chart it will be seen that a rough division may be made of systems ordinarily called emulsions, into mechanical suspensions and true emulsions, the former being characterized chiefly by a greater instability; the latter being characterized by extreme stability which is in general produced by the presence of an effective emulsifying agent. It is realized, however, that no sharp line of demarcation may be drawn between the two. This investigation deals only with true emulsions.

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[1] Presented at the Symposium on Emulsification Problems in the Petroleum Industry before the Section of Petroleum Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[2] Published as Contribution No. 41 from the Research Laboratory of Applied Chemistry, Massachusetts Institute of Technology, Cambridge, Mass.

A division of true emulsions into the two types, namely, oil-in-water and water-in-oil, is made and a general classification of the emulsifying agents which tend to produce these types, together with the various methods of breaking the emulsions, is indicated. In general, the emulsifying agents which tend to produce an oil-in-water type are those which are either soluble in water, the external phase, or which are more readily wetted by water than by oil. Correspondingly, in the case of the water-in-oil type of emulsions, solubility or greater wetting of the oil phase by the emulsifying agent is the necessary prerequisite. The present generally accepted theory of the formation of emulsions postulates the presence of a stabilizing film around the particles of the dispersed phase which prevents their coalescing. Although the exact nature of this viscous film is not clearly known, it is evident, as stated by Bancroft,[1] that the type and properties of the emulsions depend largely on the nature of this viscous film. Some work in this Laboratory[2] indicates that this film possesses the properties of a plastic solid. If the emulsifying agent could be altered so that it was wetted more by the internal phase, the emulsion should invert. Clowes[3] supported this theory and was able to change an oil-in-water emulsion stabilized by sodium oleate to a water-in-oil type by the addition of a calcium salt which formed the oil-soluble soap which is insoluble in water. Clowes further stated that when the equivalent ratio of sodium to calcium was 4 : 1, the effects were balanced and neither kind of emulsion was formed. These results were obtained from a study of emulsions of olive oil[4] which, on account of its composition and the impurities present in it, undoubtedly behaves differently from mineral oils. Bhatnagar[5] found that the 4 : 1 ratio above mentioned was affected by the volume ratio of the two phases as well as by other ions and that it changed with different soaps. In previous work in this Laboratory no critical ratio was found when magnesium and sodium oleates were used as emulsifying agents in the case of emulsions with Nujol.

It has been said that the inversion of phases could be effected by increasing the amount of dispersed phase until a critical point was reached where the dispersed phase became the continuous one. This point was supposed to be near the 74 per cent stable emulsion as described by Ostwald.[6] Pickering's[7] highly concentrated emulsion disproved this theory to some extent. Inversion by increasing the amount of dispersed phase implies that the emulsifying agent could stabilize either form of emulsion, forming a protective film about the small particles of either phase. This obviously opposes the Bancroft theory of emulsification and would tend to contradict the theories of Bancroft and Clowes as to the specific tendency of emulsifying agents to form one or the other type of emulsion. According to this theory, the nature of the stabilized film would have to be changed in order to produce inversion and the only effect of increasing the ratio of the dispersed phase should be to break (not invert) the emulsion, or else to allow the excess of the disperse phase to form a separate, nonemulsified phase.

In various technical emulsions it is often difficult to determine the exact nature of the emulsifying agent. In order to control intelligently the breaking of these emulsions, it is necessary first to determine the characteristics of the emulsifying agent, then to destroy it or convert it to an ineffective form.

As indicated in Fig. 1, there are several general physical methods of breaking which may be applied to both types of emulsion. In breaking emulsions by these methods the mechanism is undoubtedly due chiefly to a rupturing or destruction of the film by physical action—for example, by electrical treatment, change of temperature, distillation, etc.

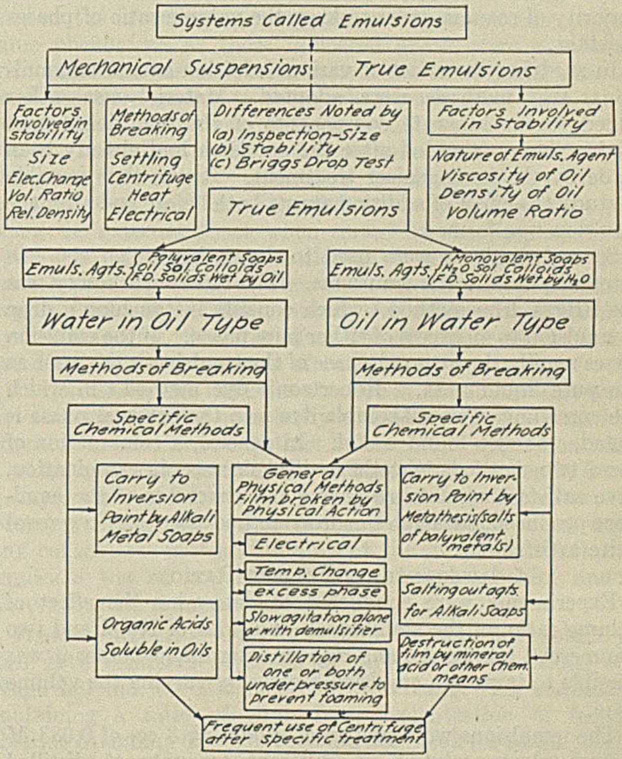

FIG. 1—GENERAL PROPERTIES OF MINERAL OIL-WATER EMULSIONS

The specific chemical methods of breaking depend for their action either on carrying the emulsion to the inversion point or on destroying the film with specific chemical reagents. In order to invert an emulsion—for example, an oil-in-water type stabilized by sodium oleate—one must, in general, add a material which is soluble in water, the external phase, since by this means alone is it possible to penetrate readily the external phase, and affect the emulsifying film. In the above-mentioned emulsion this may be readily accomplished by the addition of calcium chloride which is water-soluble and which, by metathesis, produces calcium oleate which is soluble in oil. The addition of sulfuric acid or ether is an example of a specific chemical method of destroying the film.

PREPARATION OF EMULSIONS AND METHODS OF TESTING

For the larger part of the work Nujol was selected as the oil to be emulsified. This selection was made because Nujol, although essentially a medicinal oil, has been subjected to an extremely careful process of purification similar to that given other mineral oils, and from previous work in this Laboratory has been found fairly satisfactory for experimental comparison with commercial mineral oils, especially when impurities present in or extracted from these oils have been added to it. The Nujol used was found to give practically no coloration with sulfuric acid, and also showed no tendency to give stable emulsions with water alone. Aqueous solutions of sodium oleate were used as emulsifying agents for producing the oil-in-water type of emulsion. Magnesium oleate dissolved in Nujol was typical of an oil-soluble polyvalent soap which tends to give a water-in-oil type of emulsion.

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[1] *J. Phys. Chem.*, **19** (1915), 275.

[2] *Chem. Met. Eng.*, **24** (1921), 19, 825.

[3] *J. Phys. Chem.*, **29** (1916), 407.

[4] *Ibid.*

[5] *J. Chem. Soc.*, **117** (1920), 542; **118** (1921), 61.

[6] *Z. Kolloidchem.*, **6** (1910), 103.

[7] *Koll. Z.*, **7** (1910), 11.

In preparing the emulsions the Briggs homogenizer[1] was used, with a capillary of about 1 mm. in diameter. All emulsions were prepared by first stirring vigorously for 2 min. by means of an electric stirrer and then passing the emulsion five times through the homogenizer. Microscopic examination showed that this procedure gave a uniform and fine-grained emulsion. From previous work in this Laboratory, it was decided to use equal amounts of oil and water in the majority of cases in order to keep the volume ratio of phases constant.

In studying the effect of various addition agents on emulsions, two methods were adopted. Material was either added to the separate components of the emulsion before mixing them, or added after the emulsion had already been made by the homogenizer treatment. It was thus possible to study the effect of addition agents both before and after the emulsion was formed.

Several methods were used to determine which was the external phase in the emulsions. The most satisfactory was the Briggs drop method,[2] which consists in touching a drop of emulsion to an excess of either pure phase. If the emulsion mixes readily the external phase of the emulsion is the same as the pure liquid used. Robertson's dye method,[3] in which the spreading of an oil-soluble dye into the external phase is tested, was also found useful. In general, a combination of these two methods, together with microscopic examination, gave satisfactory data regarding the character of the emulsions produced, although the drop method alone was in general quite satisfactory.

INFLUENCE OF VOLUME RATIO

Experiments were conducted to determine the effect of volume ratio on the stability of emulsions of Nujol and two commercial lubricants, and also to determine whether it was possible to invert an emulsion merely by varying the volume ratio.

The emulsions were prepared by adding 3 cc. of 0.033 M sodium oleate solution in different amounts of distilled water to the oils, varying the ratio of volumes of oil and water but keeping the total volume at 50 cc.

A maximum ratio of volume of oil to total volume of emulsion was found which gave a homogeneous oil-in-water emulsion. Above this value, which was 0.84 for Nujol and 0.83 and 0.87 for the other lubricants tested, a more fluid mixture was obtained which, on testing by the drop method immediately after mixing, appeared to be a water-in-oil emulsion. The mixture usually settled to three layers. The top layer contained some water dispersed in oil, but the drops were large enough to be visible to the naked eye, indicating a mechanical suspension rather than a true emulsion. The second layer was always too thin for satisfactory testing but appeared similar to the oil-in-water emulsions which resulted when the volume ratio was below the critical value. The lower layer consisted of excess water. After standing for some time the drops of water frequently settled out of most of the upper oil phase, leaving a clear layer of oil at the top.

It will be noted that the above critical values are all somewhat higher than the 74 per cent which represents the amount of interior phase which is possible with close packed spheres. The amount of excess emulsified above 74 per cent is therefore more or less of a measure of the ability of the films to resist rupturing when further and further distorted from their normal spherical shape.

In general, therefore, no true inversion point was noticed when the volume ratio alone was varied in the case of the three oils studied, but, as would be expected, there was a maximum amount of oil which could be emulsified by sodium oleate. Above this point, which was well defined for each oil, breaking occurred. This contradicts certain of the above-mentioned experimenters, but confirms the conclusions of Bancroft and Clowes. In order to eliminate the effect of volume ratio in subsequent experiments, the ratio of oil to total volume of emulsion was kept constant at 0.5, thus choosing a region in which the oil-in-water emulsions of Nujol would be fairly stable.

OPPOSING EMULSIFYING AGENTS IN DIFFERENT PHASES

An interesting series of emulsions was studied in order to determine the effect of opposing emulsifying agents, such as sodium oleate and magnesium oleate, which tend to produce oil-in-water and water-in-oil emulsions, respectively. The general method of experimentation was to shake a solution of sodium oleate in water with a solution of magnesium oleate in Nujol, keeping the volume ratio 50 : 50. A large number of emulsions were studied, varying the ratio of equivalent concentration of magnesium oleate to sodium oleate from 25 to 0.54. It was desired to obtain the characteristics of the above system when both emulsifying agents were present, in order to determine whether a real equilibrium existed and whether there was some critical ratio of the emulsifying agents at which point no emulsion at all would be formed.

In all cases the resulting emulsions settled out in three layers, oil on top, water on the bottom, and varying amounts of emulsion between. This middle emulsion layer was tested at different levels by withdrawing a portion by means of a capillary pipet and applying the drop test. In many cases both types of emulsion were found, water-in-oil in the upper portion and oil-in-water in the lower portion. After standing for several days a distinct line of demarcation was noticed in this emulsion layer, above which the drop test indicated the presence of a water-in-oil and below an oil-in-water emulsion.

This phenomenon was noticed in six emulsions in the series studied, where the ratio of magnesium oleate to sodium oleate varied from 1.0 to 10, and is now being very carefully investigated. It appears that an equilibrium is set up between the two types of emulsions and that, on standing, the less stable water-in-oil emulsion, which is much coarser grained than the oil-in-water, apparently undergoes gradual breaking, with the separation of oil. In the above experiments the systems were prepared in several different ways. In some cases an oil-in-water emulsion was made and then treated with magnesium oleate; in others, the water-in-oil was prepared and treated with sodium oleate; in others, a solution of sodium oleate in water and of magnesium oleate in oil were mixed simultaneously, all of the above series being put through the homogenizer. The presence of both types of emulsion was independent of the method of preparation.

Although the above series is being subjected to more critical investigation on account of the interesting characteristics observed, it appears that no ratio of magnesium oleate to sodium oleate was found where the opposing forces were balanced, giving an inversion point with no stable emulsion, but rather that some form of pseudo-equilibrium was set up whereby *both* types of emulsion were produced.

INVERSION BY METATHESIS

A study was made of the effect of aqueous solutions of various divalent and trivalent salts on the stability and tendency to invert of oil-in-water emulsions of Nujol. The oil-in-water emulsions were made in the usual way by stirring and homogenizing, using sodium oleate as the emulsifying agent. Aqueous solutions of magnesium sulfate, magnesium chloride, and ferrous sulfate were added in varying concentration as typical representatives of bivalent salts, and alu-

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[1] *J. Phys. Chem.*, **19** (1915), 223.

[2] Newman, *Ibid.*, **18** (1914), 34.

[3] *Kolloid. Z.*, **7** (1910), 7.

minium sulfate and ferric chloride in aqueous solution were the addition agents typical of the trivalent salts. The volume ratio of oil to total emulsion in the resulting mixture was 0.5 in each case.

MAGNESIUM SALTS—It was found that if the equivalent concentration of magnesium was greater than that of sodium a complete inversion to the water-in-oil type resulted. In cases where the amount of magnesium salt was not sufficient to react with all of the sodium oleate, both types of emulsions were formed. The general appearance and properties of the latter emulsions were similar to those of the emulsions described above in the series on opposing emulsifying agents. In order to show definitely that the determining factor was the ratio of equivalents of magnesium to sodium rather than the absolute concentration of these substances, several runs were made in which the absolute concentration of magnesium salt was lower than that which had failed to invert completely in previous cases, reducing the sodium until it also was less than the magnesium. A complete inversion of the emulsion resulted, indicating the ratio to be the determining factor rather than the absolute concentration of magnesium sulfate added. Comparison of Emulsions 53 and 66 in Table I indicate the results above described.

The effect of using magnesium chloride was very similar to that of the magnesium sulfate and no indication was obtained of any appreciable variation in the inversion point due to a variation in the anion of the magnesium salt.

TABLE I—INVERSION BY METATHESIS

System—Sodium oleate in water, Nujol and $MgSO_4$ in water
$MgSO_4$ = addition agent

No.	Method of Mixing	Vol. Ratio	Equiv. Conc. NaOl = A	Equiv. Conc. $MgSO_4$ = B	$\frac{B}{A}$	External Phase Final Emulsion	REMARKS
50	Added	0.5	0.0279	0.32	11.5	Oil	Complete inversion
51	Added	0.5	0.0293	0.24	8.2	Oil	Complete inversion
52	Added	0.5	0.0306	0.16	5.2	Oil	Complete inversion
53	Added	0.5	0.0319	0.08	2.5	Oil	Complete inversion
54	Added	0.5	0.0266	0.04	1.5	Oil	Complete inversion
71	Added	0.5	0.0266	0.0266	1.0	Both	Very indistinct layers
55	Added	0.5	0.0293	0.024	0.82	Both	Partial inversion
56	Added	0.5	0.0306	0.016	0.52	Both	Partial inversion
66[1]	Added	0.5	0.0064	0.016	2.5	Oil	Complete inversion

[1] Shows that ratio of equivalents was the determining factor rather than absolute concentration.

TABLE II—INVERSION BY METATHESIS

System—Sodium oleate in water, Nujol and $MgCl_2$ in water
$MgCl_2$ = addition agent

No.	Method of Mixing	Vol. Ratio	Equiv. Conc. NaOl = A	Equiv. Conc. $MgCl_2$ = B	$\frac{B}{A}$	External Phase Final Emulsion	REMARKS
65	Added	0.5	0.0253	0.48	19.0	Oil	Complete inversion
64	Added	0.5	0.0279	0.32	11.5	Oil	Complete inversion
63	Added	0.5	0.0306	0.16	5.2	Oil	Complete inversion
62	Added	0.5	0.0266	0.04	1.5	Oil	Complete inversion
72[1]	Added	0.5	0.0266	0.0266	1.0	Oil	Complete inversion
61	Added	0.5	0.0306	0.016	0.52	Both	Partial inversion
60	Added	0.5	0.0319	0.008	0.25	Both	Partial inversion

[1] Compare with (71) in the preceding table. See discussion of metathesis.

The behavior of the solution during inversion was very interesting. When magnesium salt was added to an oil-in-water emulsion the viscosity was very greatly lowered while the salt was being added. Then the mixture became more viscous than the original emulsion, with oil appearing to be the external phase. It is possible that the magnesium first reacted with the sodium soap in the film and caused a temporary breaking of the emulsion, since the two phases formed a mixture possessing none of the high viscosity ordinarily characteristic of emulsions. The magnesium oleate formed by metathesis was then dissolved by the oil and on solution in the oil tended to disperse the water, giving a high viscosity characteristic of a true emulsion.

It should be noted that in the above cases no really sharp inversion point was obtained, but rather the presence of an unstable period of time during which inversion occurred.

FERROUS SULFATE—Since ferrous sulfate has been suggested as a demulsifier,[1] the effect of adding a solution of this salt to Nujol oil-in-water emulsions was investigated. In every case where the ratio of the equivalent concentration of ferrous sulfate to sodium oleate was above 1 an inversion was effected followed by a distinct breaking of the emulsion. This is essentially due to the weak emulsifying tendency of the iron soap produced by metathesis.

ALUMINIUM SULFATE—Aluminium sulfate in water was used as the inverting agent typical of a trivalent salt. The same phenomena as those indicated above were observed with regard to viscosity changes. Undoubtedly the effects produced were similar to those when magnesium salts were added, although the final result was modified somewhat by the extreme instability of the water-in-oil emulsions produced by the aluminium soap. Immediate breaking occurred to a certain extent, and the liberated water gave the effect of being the external phase when tested by the drop method before the emulsion had settled in layers. Complete inversion probably resulted when the concentration of aluminium sulfate was sufficient, but it was followed so quickly by breaking that the latter effect was the major one as indicated by the usual methods of testing.

In one case where the concentration of aluminium salt was not sufficient to react completely with the sodium oleate, the emulsion formed in two distinct layers. The upper one was a water-in-oil emulsion which was completely broken in 3 or 4 days, while the lower, in which water was the external phase, remained dense and unchanged for some time. At any concentration of addition agent the instability of these emulsions was an important factor although breaking must have occurred after inversion.

FERRIC CHLORIDE—Ferric chloride in aqueous solution also gave complete inversion of oil-in-water emulsions of Nujol but did not always produce breaking. An emulsion containing a ratio of equivalent concentration of ferric chloride to sodium oleate of 7.52 did not break for 24 hrs., and one whose ratio was 1.21 remained one of the most stable water-in-oil emulsions studied.

CONCLUSIONS—Fig. 2 shows a graphical summary of the results above indicated. In general the following conclusions may be drawn regarding the inversion of oil-in-water emulsions of Nujol by means of metathesis:

1—Divalent or trivalent salt dissolved in water could completely invert oil-in-water emulsions.

2—In the limited range studied, namely, in the case of magnesium chloride and magnesium sulfate, there is apparently very little effect due to a variation in the anion of the added salt.

3—In inversion by metathesis the ratio of equivalents of the inverting agent to the emulsifying agent was the determining factor rather than the absolute concentration of the former.

4—When the equivalent concentration of the polyvalent salt exceeded the monovalent, complete inversion took place. When it was less than the monovalent, a pseudo-equilibrium was established whereby some of both types of emulsion was produced.

5—The mechanism of the above inversion indicated first a chemical reaction destroying the film, then breaking the emulsion and forming the polyvalent soap, and finally solution of the polyvalent soap in the oil and emulsification with the phases inverted.

6—In general, sodium oleate, a monovalent soap, produced more stable emulsions than the polyvalent soaps in the case of Nujol systems. Of the polyvalent soaps studied magnesium oleate apparently gave the greatest stability.

SALTING OUT OF EMULSIONS

A brief study of the so-called "salting out" of emulsions was made in the case of oil-in-water emulsions of Nujol where

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[1] U. S. Patent 1,093,098.

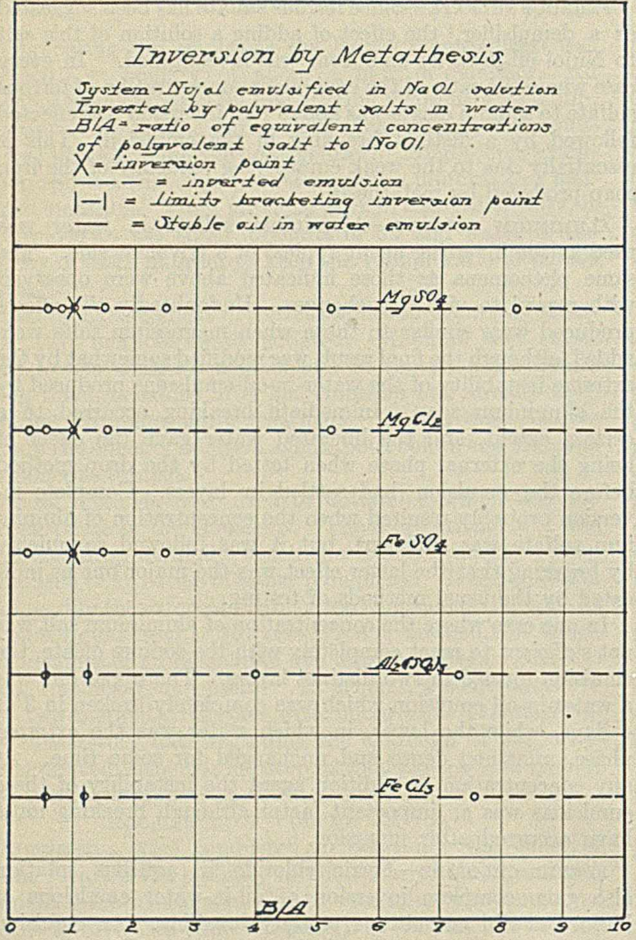

FIG. 2

sodium oleate was the emulsifying agent. Sodium chloride, iodide and sulfate were added in varying concentrations keeping the volume ratio always 0.5. One series was also studied where sodium chloride was added to a water-in-oil emulsion of Nujol produced by magnesium oleate.

TABLE III—SALTING OUT EMULSIONS—SODIUM CHLORIDE

System—Sodium oleate in water, Nujol and NaCl in water
NaCl in water = addition agent

No.	Method of Mixing	Vol. Ratio	Equiv. Conc. NaOl = A	Equiv. Conc. NaCl = B	$\frac{B}{A}$	External Phase Final Emulsion	REMARKS
35	Added	0.5	0.0173	0.48	27.7	None	Broke immediately
36	Added	0.5	0.0200	0.40	20.0	None	Broke immediately
37[1]	Added	0.5	0.0240	0.28	11.7	None	Broke immediately
44	Added	0.5	0.0253	0.24	9.1	None	Broke immediately
48	At once	0.5	0.0253	0.24	9.1	None	Broke immediately
45	Added	0.5	0.0259	0.22	8.5	None	Broke after some time
49	At once	0.5	0.0259	0.22	8.5	None	Broke after some time
38	Added	0.5	0.0266	0.20	7.5	Water	Creamed to two layers
47	At once	0.5	0.0266	0.20	7.5	Water	Creamed to two layers
39	Added	0.5	0.0280	0.16	5.7	Water	Creamed to two layers
46[1]	Added	0.5	0.0120	0.14	11.7	Water	Creamed to two layers
40	Added	0.5	0.0293	0.12	4.1	Water	Creamed to two layers
41	Added	0.5	0.0307	0.08	2.5	Water	Creamed to two layers
42	Added	0.5	0.0320	0.04	1.25	Water	Creamed to two layers
43	Added	0.5	0.0333	0	0	Water	Creamed to two layers

[1] Shows that conc. B determines salting out effect: compare Nos. 37 and 46.

The experimental results may be seen by reference to Tables III, IV, and V. Sodium chloride solution above a definite concentration broke the emulsions almost completely, but no indication of inversion was found. A concentration of 0.24 *M* sodium chloride was sufficient to break the emulsions immediately and a 0.22 *M* had the same effect after a few days. Below this value perfectly stable emulsions were produced. By comparing Emulsions 46 and 37 in Table III the effect of absolute concentration and ratio of concentration of emulsifying agent to addition agent may be seen. It was not possible to break the emulsion in (46) by decreasing the concentration of both sodium chloride and sodium oleate and still keeping a high ratio of chloride to oleate. This indicates that the absolute concentration of sodium chloride is the determining factor in breaking these emulsions.

TABLE IV—SALTING OUT EMULSIONS—SODIUM IODIDE

System—Sodium oleate in water, Nujol and NaI in water
NaI = addition agent

No.	Method of Mixing	Vol. Ratio	Equiv. Conc. NaOl = A	Equiv. Conc. NaI = B	$\frac{B}{A}$	External Phase Final Emulsion	REMARKS
120	Added	0.5	0.0240	0.28	11.7	None	Broke immediately
121	Added	0.5	0.0253	0.24	9.1	None	Broke immediately
122	Added	0.5	0.0259	0.22	8.5	None	Broke immediately
123	Added	0.5	0.0266	0.20	7.5	None	Broke immediately
125	Added	0.5	0.0273	0.18	6.6	None	Broke immediately
124	Added	0.5	0.0280	0.16	5.7	Water	Stable

TABLE V—SALTING OUT EMULSIONS—SODIUM SULFATE

System—Sodium oleate in water, Nujol and Na_2SO_4 in water
Na_2SO_4 = addition agent

No.	Method of Mixing	Vol. Ratio	Equiv. Conc. NaOl = A	Equiv. Conc. Na_2SO_4 = B	$\frac{B}{A}$	External Phase Final Emulsion	REMARKS
151	Added	0.5	0.0247	0.26	10.5	None	Broke immediately
150	Added	0.5	0.0253	0.24	9.1	None	Broke
152*a*	Added	0.5	0.0259	0.22	8.5	Water	Stable

Oil-in-water emulsions of Nujol were also broken by 0.18 *M* sodium iodide and 0.24 *M* sodium sulfate, indicating a slight variation, as near as experimental conditions could determine, in the minimum breaking concentrations due to a variation in the anion of the sodium salt used. The results obtained may be seen in Tables IV and V.

Indefinite results were obtained in investigating the salting-out effect of sodium chloride on water-in-oil emulsions of Nujol where magnesium oleate was the emulsifying agent. On account of the inherent instability of these emulsions breaking took place very easily and obscured the effect of the salt alone. It should be expected, however, that an aqueous solution of a salt would not give a well-defined reaction with water-in-oil emulsions on account of the inability of the salt in the aqueous phase to get at the emulsifying film, since in the case of water-in-oil emulsions the external phase is oil.

Generally speaking, to influence the properties of a particular film of emulsifying agent any substance which is added should be soluble in, or wetted by, the external phase of the emulsion in question. In this connection the following experiment is of interest.

A colloidal suspension of magnesium oleate in water was obtained by dissolving the oleate in acetone and adding the solution to a large quantity of water. On treating an oil-in-water emulsion of Nujol (sodium oleate as the emulsifying agent) with this colloidal suspension partial inversion took place with subsequent breaking of the emulsion. This was to be expected in view of the greater tendency of the magnesium oleate in colloidal suspension in one phase to dissolve in the other phase and exert its emulsifying action.

In general, from the above series of experiments on salting out, it was found that neutral monovalent salts, such as sodium chloride, iodide, and sulfate, gave no noticeable inverting action on oil-in-water emulsions of Nujol, but broke the emulsions by salting them out when the salt concentration was sufficiently high. The salting-out effect was a function of the concentration of salt added and not of the ratio of the concentration of salt to emulsifying agent.

In contrast to inversion by metathesis, the anion here appeared to have an appreciable effect, the minimum salting-out concentration being as follows: for sodium sulfate, 0.24; sodium chloride, 0.22; sodium iodide, 0.18.

In connection with future work on salting out of emulsions, it is planned to undertake a more thorough investigation of the mechanism of breaking emulsions by salting out with particular reference to the following points: The relation between the concentration of the salting-out substances and the concentration of emulsifying agent, a more complete study of the effect of various anions, a search for some oil-soluble "salting-out" agents, the general application of salting-out processes on a commercial scale, and a study of the development of the sodium chloride method for breaking emulsions as a laboratory tool for investigation.

EFFECT OF ADDITION AGENTS ON STABILITY OF EMULSIONS

As a second phase of the present investigation it was desired to ascertain the effect on the properties of oil-in-water emulsions of Nujol produced by sodium oleate of adding to these emulsions various substances known to be present in, or to exert an influence upon, emulsions met with in practice. The Nujol was emulsified in the usual manner with sodium oleate, and the stabilizing action of the added substance was measured by determining the concentration of sodium chloride solution necessary to break the emulsion. Although this sodium chloride treatment is rather an arbitrary test of stability, nevertheless it has been found to represent a fairly definite break point for other emulsions as well as Nujol. In every case the volume ratio was kept at 0.5 and the equivalent concentration of sodium chloride solution necessary to break the emulsion was recorded. The results are indicated in Fig. 3. Different methods were employed for adding the substances under investigation to the emulsions, varying according to the nature of the material used.

Since various sulfonates which are produced during the acid treatments of oils in the refining process exert a certain influence on the emulsifying tendencies of the oil, substances representative of this class of materials were added to Nujol, the resultant oil was emulsified, and the break point was determined by addition of sodium chloride solution. The substances used included pure sodium benzenesulfonate, the sodium salt of a sulfonated oil isolated from the acid treatment of a Texas oil, and the alcoholic extract from an acid-treated oil which in addition to containing various sulfonates contained certain amounts of sodium naphthenates. The sodium benzenesulfonate and the alcoholic extracts were added directly to the Nujol, whereas the sodium salt of the sulfonated oil was first dissolved in ether, then added to Nujol, and the ether evaporated. From Fig. 3 it is evident that the substances of this class have only a very slight effect, if any, on stabilizing oil-in-water emulsions of Nujol, as evidenced by the slightly higher equivalent concentration of sodium chloride necessary to break the emulsion.

Colloidal coloring matter obtained from a heavy lubricating oil was dissolved in ether and added to Nujol, and after removal of the ether by evaporation, the emulsifying tendency of the resultant mixture was determined. The sodium chloride necessary to break this emulsion was 0.24 *M*, practically the same as that required for the emulsion of Nujol alone. This indicates practically no effect of the colloidal coloring matter on the stability of the emulsion, at least as determined by the salting-out action of sodium chloride.

Since previous work in this Laboratory has indicated that amylene gives somewhat analogous results to other unsaturated bodies which are present in oils, the stabilizing action of amylene when added in various amounts of oil-in-water emulsions of Nujol was investigated. From Fig. 3 it is evident that the equivalent concentration of sodium chloride necessary to break these emulsions was much higher than when other substances were added to the Nujol. This indicates a marked stabilizing action on oil-in-water emulsions of Nujol by amylene, and it is interesting to note that the points thus determined fall on a fairly smooth curve. The significance of this curve, however, has not yet been clearly established, but is being subjected to further investigation. Although amylene and water give a rather unstable emulsion, the tendency of the amylene is toward stabilizing an emulsion of the oil-in-water type.

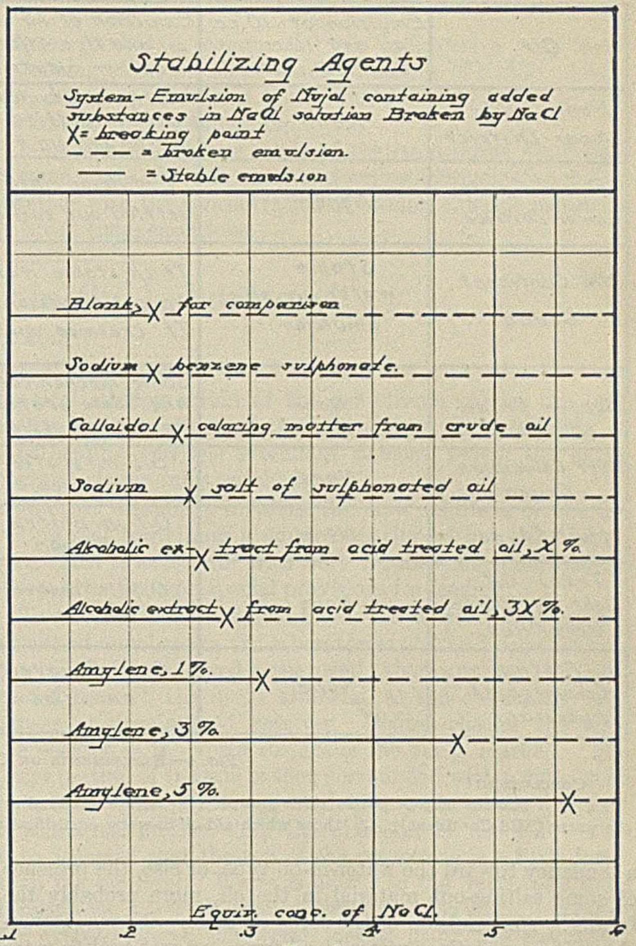

FIG. 3

In general, as indicated in Fig. 3, amylene is the only substance which exerts an important stabilizing effect when added to oil-in-water emulsions of Nujol. Other substances known to be present in commercial oil exert a very slight, if any, stabilizing action. This stabilizing action is determined by means of the concentration of sodium chloride necessary to break the emulsion.

INVESTIGATION OF COMMERCIAL OIL EMULSIONS

Several crude oils and a commercial lubricant were emulsified with sodium oleate in order to determine the stability of the emulsions thus produced, and also the concentration of sodium chloride necessary for breaking them. These crude oils were received directly from the wells and contained all the impurities common to their respective localities, having been subjected to no refining process. The oils were first agitated with an equal volume of distilled water to discover any emulsifying action of the oil with water, and 15 cc. of the oil were then emulsified with 11 cc. of 0.033 *M* sodium oleate. Two samples were made of the latter. One was allowed to stand untreated and the other was salted out with sodium chloride. The results are indicated in Fig. 4.

In the emulsion of the Upper District Pennsylvania crude with sodium oleate, a very unstable system similar to a mechanical suspension was formed. This could be accounted for in two ways: either something present in the oil reacting with the sodium oleate to produce an emulsifying agent with

Oil	Emulsion of 10 c.c. oil and 10 c.c distilled water	Emulsion of 15 c.c oil and 11 c.c M/30 sodium oleate	Equiv. conc NaCl for immediate breaking.	Remarks
Penn. Crude Upper District	None	Mostly mechanical suspension. Settled out by self in time.	.27 Oil layer not clear.	See discussion. Oil may contain opposing or salting out substances.
Penn. Crude Lower District	None.	Emulsion all settled out easily.	.24	The sodium oleate emulsion settled out very completely without any salt added.
Mid-Continent Crude	Stable water in oil emulsion	Thick, stable water in oil emulsion. It creamed down.	.45	Due to 1. NaCl inefficient for this type. 2. The blank was very stable. 3. End point hard to see due to dark color.
Ranger Crude	None	Some mechanical and some water in oil emulsion	.27	Oleate emulsion separated out by itself a little.
West Columbian Crude	None	Oil in water emulsion.	.35	
Hull Crude	None	Oil in water emulsion	.31 Water layer opaque	
Texas Oil Light Distillate Unrefined	None	Oil in water emulsion	.32	
Arctic, Commercial Lubricant	None	Oil in water emulsion	.28	

FIG. 4—EXPERIMENTS ON CRUDE AND COMMERCIAL OILS

CONCLUSION:

The oils may be put in three groups: (1) those which tend to resist emulsification (both Penn. oils and Ranger); (2) those which disperse the water (Mid-Continent); (3) those which aid oil-in-water emulsification (all others listed).

a tendency toward the water-in-oil type, or else, the presence of some salting-out material in the oil, more probably the former. An emulsion of the same oil made with magnesium oleate gave a distinct water-in-oil type, but was broken more easily than the one made with sodium oleate. The oil therefore had no particularly strong tendency to become the external phase, but merely resisted emulsification of any type. A similar effect was noticed in the case of the Lower District Pennsylvania crude. In all cases the mixtures formed were very unstable, requiring a slightly lower concentration of sodium chloride to salt out than was true in the case of the Upper District oil.

It will be noticed in the case of the Mid-Continent crude that with water alone a water-in-oil emulsion is obtained, whereas when the oil is treated with sodium oleate there is still a tendency toward production of a water-in-oil type. This oil obviously contains some emulsifying agent tending to produce a fairly stable water-in-oil type and requiring a fairly high concentration of sodium chloride for breaking. A similar tendency toward a water-in-oil type was noted in the case of the Ranger crude when emulsified with sodium oleate.

The last four oils listed in the chart behaved very similar to Nujol. No emulsion was formed with water but a fairly stable oil-in-water emulsion was produced with sodium oleate and was easily broken by a moderate concentration of sodium chloride.

The above series of observations, although limited in scope, indicate some of the simplest characteristics of these oils when treated with sodium oleate and broken with sodium chloride. The exact mechanism and behavior of this sodium chloride treatment is being further investigated and the range of applicability of this method as a laboratory tool is being determined.

CONCLUSIONS

1—This investigation covers some preliminary results obtained in a study of the factors influencing the stability and inversion point, in emulsions of Nujol and water, and then in Nujol-water emulsions to which substances present in commercial oils have been added. A comparison of the properties of the above systems with different commercial oils is made. Although most of the results obtained relate specifically to emulsions of Nujol, some fundamental observations have been made which, when extended, should throw considerable light on the problems involved in the stability of commercial emulsions.

2—No true inversion point was noted when the only variable was the ratio of the volume of the two phases.

3—In studying the effect of opposing emulsifying agents by mixing solutions of sodium oleate in water with magnesium oleate in oil, no sharp inversion point was found, but a pseudo-equilibrium appeared to be established, some of both types of emulsion being indicated by the drop test. These emulsions were frequently separated by a sharp line of demarcation. This appears to be contradictory to some results in the literature, though the experiments were not strictly analogous.

4—The following divalent and trivalent salts in aqueous solution were able completely to invert oil-in-water emulsions of Nujol by metathesis: $MgSO_4$, $MgCl_2$, $FeSO_4$, $Al_2(SO_4)_3$, $FeCl_3$. In this metathesis the ratio of equivalents of metallic precipitating ions was the determining factor rather than their absolute concentration. When the equivalent concentration of polyvalent metal exceeded that of monovalent soap, complete inversion resulted. When it was less, there was partial inversion similar to that above described, both types of emulsions apparently being present. The probable mechanism of this metathetical inversion is discussed. Variation in the anions of the precipitating salts studied had no appreciable effect on the results.

5—Neutral monovalent salts such as sodium sulfate, sodium chloride, and sodium iodide had no inverting action on oil-in-water emulsions, but when present in sufficient concentration broke the emulsion, presumably by "salting out" the soap film. This salting-out effect was a function of the salt concentration, not of the ratio of concentrations of salt to soap. A variation in anion appeared to have some effect in inversion by salting out, the minimum salting-out concentration in equivalents being as follows: Sodium sulfate, 0.24; sodium chloride, 0.22; sodium iodide, 0.18.

6—A study of the effect of the addition of certain substances present in commercial oils indicated a very weak stabilizing effect on oil-in-water emulsions of Nujol. Amylene, however, stabilized these emulsions somewhat in proportion to its concentration.

7—A brief study was made of the emulsifying tendencies of some crude oils with water and with sodium oleate solution together with the concentration of sodium chloride necessary to break these emulsions.

The Dehydration of Tar in the Laboratory[1]

By Wilbert J. Huff

The Koppers Company Laboratories, Mellon Institute, Pittsburgh, Pa.

The condensing systems which remove most of the tar from gas generally chill this gas well below its dew point; consequently raw tar usually contains considerable water. Subsequently the water content is usually reduced to a few per cent by gravity separation but this separation is never complete and in the case of very viscous tars, such as certain coal tars and tars having a gravity close to that of water, such as certain water-gas tars, the gravity separation is very unsatisfactory and some tars retain a very high percentage of water after standing indefinitely. For this reason, tars are generally held to be emulsions. Any tar containing more than a few tenths of a per cent water, if heated rapidly, may foam or bump badly. Consequently the elimination of the water is an extremely important problem for the tar distiller and the chemist engaged in the examination of tars.

For the dehydration of tar and other organic emulsions, a large number of procedures have been proposed.[2] In general the laboratory methods involve distillation following the addition of a solvent, or surface evaporation. The removal of water by centrifuging or by electrostatic attraction is not complete, and these methods are, therefore, not generally used in the laboratory. Grinding with carbon black and centrifuging with a solvent permit the rapid estimation of water,[3] but present the disadvantage that the tar residue cannot conveniently be used for further study. Methods which involve the addition of a suitable solvent and distillation, such as for instance the excellent method of Dean and Stark,[4] do not permit the determination of the light oil on the same portion of the sample and are generally not used when the chief object is the complete examination of the distillates and pitch.

For such studies, resort is had to surface evaporation processes which involve heating the tar from above, usually with a ring burner.[5,6] These methods, however, present the disadvantage that the heat is generally not confined to the upper portions of the tar; consequently many tars froth and spatter disastrously in spite of the most exacting care on the part of the operator. A current of gas[7] is sometimes passed through the tar to overcome this disadvantage; but this expedient is not ideal, because the gas current, unless chilled to low temperatures, will carry away uncondensed vapors of water and light oils. Moreover, the mechanical stirring action of the gas stream carries the heat to the lower portions of the still charge, thus assisting in superheating and the attendant dangers unless the entire operation is carefully watched.

Another expedient involves the slow addition of the tar to the still containing a small quantity of hot dehydrated tar. This is successful with very troublesome tars, but requires attention and special provisions for feeding.

To obviate these disadvantages, the writer has suggested a method now used in the laboratories of The Koppers Company. The tar is placed in the usual laboratory tar still, connected through the usual stillhead to the customary condenser and graduated receiver. Before closing the still, the position of the upper surface of the tar is marked. The lower portion of the still is then surrounded with a cylindrical receptacle open at the top—such as a pail—whose diameter is somewhat greater than the diameter of the still. This is so adjusted that the top of the receptacle is a little lower than the tar level. Water is added to the receptacle until it overflows. Heat is applied directly to the shallow layer of tar exposed above the water jacket, using the customary ring burner. This portion of the tar soon attains a temperature above the boiling point of water and the steam passes into the hot space above, where it cannot condense without passing out of the still. The water jacket absorbs heat which would otherwise be transmitted to the lower portions of the tar; consequently these are not heated above the steam point and no spattering or disastrous frothing can occur. The level of water falls gradually by evaporation, permitting the dehydrating zone to fall slowly. At any one time, the layer of *wet* tar heated sufficiently to cause steam formation is relatively shallow, consequently the steam has an opportunity to pass off quietly. When the water level has fallen below the bottom of the still, the tar is practically dehydrated. The receptacle for water is then removed, and the distillation is continued as usual.

The method is so simple that the writer finds it difficult to believe that it has not been used before, but if so, he is unaware of such use. It permits the approximate determination of light oil and water on the same portion of the sample, requires no new apparatus and practically no attention, handles efficiently very stiff tars and tars of high water content, and can be applied with advantage to the laboratory distillation of most tars.

In common with other surface evaporation methods which use direct flame heating, this may be subjected to the criticism that superheating of the vapor space may induce cracking. However, it presents the important advantage that the initial heating takes place at the tar level when the heat capacity of the tar assists in preventing the attainment of unduly high temperatures. The criticism can be eliminated by jacketing the upper portion of the still with material of high heat capacity. However, under the most unfavorable conditions the error introduced by such cracking is problematical, and it is generally disregarded.

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

[2] It is beyond the scope of this article to list these. Most of the important references have been listed by Dean and Stark, This Journal, **12** (1920), 486.

[3] Odell and Thiele, *Gas Record*, March 23, 1921, p. 30.

[4] *Loc. cit.*

[5] Senger, *J. Gasbel.*, **45** (1902), 841; also *J. Soc. Chem. Ind.*, **21** (1902), 1475.

[6] Jayne, *J. Am. Chem. Soc.*, **25** (1903), 814.

[7] If gas is used, it should be inert. The practice of blowing air through tar should of course be avoided, for tar at elevated temperatures may absorb oxygen, and with some tars, the absorption of oxygen is accompanied with a marked diminution in the quantity of recoverable oils.

Benzenedisulfonic Acid from Benzenemonosulfonic Acid[1,2]

By C. E. Senseman

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Of the several methods described in the literature for the preparation of benzenedisulfonic acid but few are specific in all details, such as concentration of acid, amount of acid, temperature, and time of heating. Barth and Senhofer[3] in 1875 described a method of sulfonating the monosulfonic acid by heating for 2 hrs. with an equal volume of fuming sulfuric acid. They neglected to record the strength of acid and proper temperature for carrying out the reaction. Koerner and Monselise[4] prepared the disulfonic acid by heating four volumes of an acid mixture, resulting from sulfonating benzene, 3 to 5 hrs. with three volumes of fuming sulfuric acid at 200° to 245°. Binschedler and Busch[5] described a method in which 24 kg. of benzene are added in a thin stream to 90 kg. of fuming sulfuric acid. The temperature is raised to the boiling point of benzene and continued for 2 to 3 hrs., during which time the mono-acid is formed. The temperature is then raised to 275° and continued for 20 min. Lambert's patent[6] specifies the heating of sodium benzene sulfonate with 1.5 times its weight of $NaH_3(SO_4)_2$ 2 to 3 hrs. at 200° to 240°. None of these investigators have reported either the yield of disulfonic acid or its ratio to the mono-acid.

In 1910 Polak[7] found that by heating 10 g. of barium benzenesulfonate with 24 cc. of 98 per cent acid at 209°, disulfonation was complete by the end of 4 hrs. The disulfonation was complete at the end of 3 hrs. when 10 g. of the barium monosulfonate were heated to 233° with 20 cc. of 12.5 per cent fuming acid.

EXPERIMENTAL

The benzenemonosulfonic acid used in this work is obtained in a crude form and purified by converting it into the barium salt by almost neutralizing with barium hydroxide and finishing off with an excess of barium carbonate.[8] After filtering, this solution is evaporated in steam evaporators and the drying completed in an electric oven at 190° for about 96 hrs. Thus prepared, the salt analyzes 99.9 per cent barium benzenemonosulfonate, the analysis being made by determining the barium present in 3 g. of the dried salt.

The apparatus used is an enameled kettle equipped with a metal bath and mechanical stirrer which has a speed of 36 revolutions per minute. An open peephole in the cover serves as an escape for steam and fumes, and also for inserting a thermometer into the sulfonating mass. About 0.5 hr. is required to bring the mixture to the desired temperature. This is not considered as a part of the total sulfonating period.

In order to determine the progress of the reaction, samples are removed in most cases at intervals of 1 hr. The sample is dissolved in water and neutralized with barium hydroxide and carbonate. From the amounts of soluble salts and barium found in an aliquot part of this solution the ratio of the disulfonic acid to the monosulfonic acid is found. In order to dry these salt mixtures completely it has been found necessary to dry them at a temperature of 190° for 72 hrs. Because of the indirect method of determining the disulfonic acid, inherent analytical errors may be responsible for differences of 1.5 per cent.

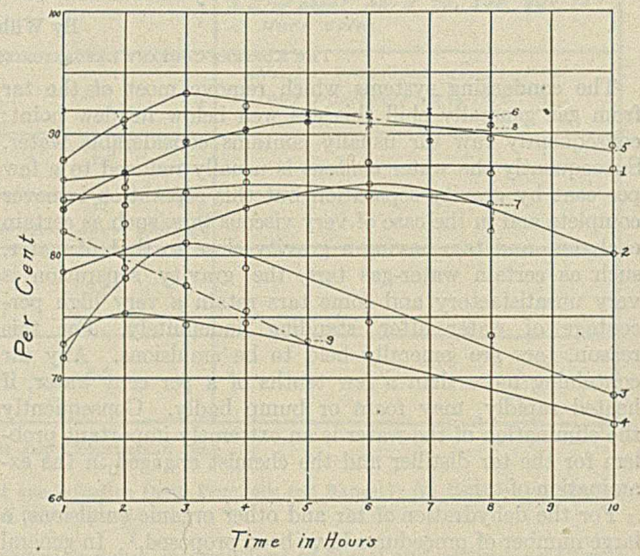

FIG. I

——— Temperature 250° C

-------- Temperature 280° C.

1—95% acid, 300% excess
2—95% acid, 150% excess
3—95% acid, 50% excess
4—95% acid, 50% excess
5—98% acid, 700% excess
6—95% acid, 150% excess, catalyst Na
7—95% acid, 150% excess, catalyst V_2O_5
8—95% acid, 150% excess, catalyst Na and V_2O_5
9—95% acid, 150% excess

In Curve 1, Fig. I, are graphically represented the results obtained by heating 1.5 moles of the dried barium benzenemonosulfonate at an average temperature of 251° for 10 hrs. with 300 per cent excess of 95 per cent acid. With this concentration and excess of acid, sulfonation is practically complete at the end of 1 hr. Table 1 gives the analytical data for this and the following eight experiments. In this work the basis for calculating the per cent excess acid is that amount of acid actually required for the sulfonation, rather than the combined amounts that are required for the sulfonation and the precipitation of the barium.[1]

TABLE 1

	Av.	Acid			Yield of Disulfonic Acid in Per cent								
EXPT.	Temp. °C.	Per cent	Excess	Catalyst	1st Hr.	2nd Hr.	3rd Hr.	4th Hr.	5th Hr.	6th Hr.	7th Hr.	8th Hr.	10th Hr.
I	251	95	300	....	86.3	85.6	....	86.8	....	87.5	....	86.6	87.0
II	250	95	150	....	78.5	82.6	....	83.8	....	85.8	....	81.9	80.1
III	252	95	50	....	71.5	78.4	81.1	78.9	....	74.5	....	73.4	68.6
IV	251	98	50	....	72.7	75.3	74.3	74.5	....	71.8	....	....	66.1
V	250	95	700	....	87.8	91.1	93.3	92.2	....	90.3	....	89.5	88.9
VI	251	95	150	Na	91.9	90.5	....	91.8	91.4	91.3	91.8	91.2	....
VII	251	95	150	V_2O_5	84.5	84.1	85.2	86.0	....	84.8	....	84.2	....
VIII	252	95	150	Na and V_2O_5	84.0	86.7	89.3	90.2	90.9	....	89.3	90.7	....
IX	279	95	150	....	81.9	78.6	77.5	75.5	73.0	....	....	....	....

The effect of lowering the amount of excess acid to 150 per cent is shown by Curve 2, Fig. I. Ninety-five per cent acid was used and an average temperature of 250° was maintained for 10 hrs. It is seen that with this amount of ex-

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[1] Presented before the Section of Dye Chemistry at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 12 to 17, 1920.

[2] Published as Contribution No. 52 of the Color Investigation Laboratory, Bureau of Chemistry, Washington, D. C.

[3] *Ber.*, 8 (1875), 1477.

[4] *Gaz. chim. ital.*, 6 (1876), 133.

[5] *Mon. Sci.*, 1878, 1169.

[6] D. R. P. 113,784 (1899).

[7] *Rec. trav. chim.*, 29 (1910), 416.

[8] Because of the difficulty encountered in securing a sufficiently high-grade barium carbonate this reagent is prepared by treating a solution of barium hydroxide with carbon dioxide until precipitation is complete. The carbonate is then thoroughly washed.

[1] Attention is called to the fact that considerable barium sulfate is held in solution by sulfuric acid of this strength. However, its effect upon the rate of sulfonation has been shown by Polak (*Loc. cit.*) to be nil.

cess acid 6 hrs. are required for the maximum production of the disulfonic acid. Further heating results in a loss of the desired product.

A further reduction in the amount of acid used gives the data for Curve 3, Fig. I, the excess acid used amounting to only 50 per cent. The acid concentration was the same as used in the two previous experiments. The average temperature for the 10 hrs. was 252°. The greatest yield of disulfonic acid was obtained after 3 hrs.' heating.

Curve 4, Fig. I, represents the results obtained when the monosulfonate is treated with 50 per cent excess of 98 per cent acid at an average temperature of 251° for 10 hrs. A slightly greater yield is obtained at the end of 1 hr. than when a 95 per cent acid is used. Further comparison is unfavorable to the 98 per cent acid, probably because the conditions are better for the carrying out of a secondary reaction which will be described later.

In obtaining the data for Curve 5, Fig. I, a much greater excess of acid has been used than for any other sulfonation, the excess amounting to 700 per cent. The acid concentration was the same as in Expts. I, II, and III, and the average temperature was 250°. The peak of the curve is reached in 3 hrs., after which time there is a slow falling off.

ADDITION OF CATALYSTS—Ambler and Cotton[1] found in their work on the sulfonation of benzene that sodium and vanadium pentoxide serve as catalysts. In Expt. VI, 0.1 per cent of the element sodium (calculated upon the weight of H_2SO_4 used) was added as Na_2CO_3. The total period of heating was 8 hrs., and an average temperature of 251° was maintained. The acid used was of 95 per cent concentration, in 150 per cent excess. Except for the addition of sodium all conditions were the same as in Expt. II. One hour's heating gave a yield of 91.9 per cent disulfonic acid, an increase of 13.4 per cent over that obtained at the end of the first hour in Expt. II. The entire Curve 6, Fig. I, is almost flat—the slight drop shown at the end of the second hour being due very likely to analytical errors.

Because of the presence of sodium in the sulfonating mass the analytical method had to be revised. After making the usual barium determination as the sulfate in a weighed quantity of the salts, sodium was determined as the sulfate by evaporating the solutions to dryness and ashing. From the weight of sodium thus found the barium equivalent was calculated, corrections made in the weight of the dried salts obtained, and the corresponding barium sulfate found.

The effect obtained by using vanadium pentoxide as a catalyst is shown in Curve 7, Fig. I. Five-hundredths per cent of the element vanadium (based upon the weight of H_2SO_4 used) was added as vanadium pentoxide. All other conditions remain the same as in Expt. VI. Again the curve obtained is almost a flat one, any one point being 6 to 7 per cent under that obtained in the previous experiment.

In Expt. VIII both sodium carbonate and vanadium pentoxide were used, 0.1 per cent of the former and 0.05 per cent of the latter. Except for an increase of 1° in the average temperature all other conditions were the same as in Expts. VI and VII. The yields throughout were below those obtained when sodium alone was used.

CHANGE OF TEMPERATURE—In Expt. IX a temperature change to 280° was made. One hundred and fifty per cent excess of 95 per cent acid was used. A comparison with Curve 2 shows that the higher temperature produces a greater amount of the acid in 1 hr., after which time there is a gradual falling off from 81.9 per cent to the 73 per cent resulting at the end of 5 hrs. At this temperature there is much charring of the materials.

SULFONATION AT 220°—In Fig. II are shown the curves which represent the results obtained by sulfonating at approximately 220°. Acid of 95 per cent concentration was used in each case, and the excess was 150 per cent. The analytical data for the four experiments are given in Table 2.

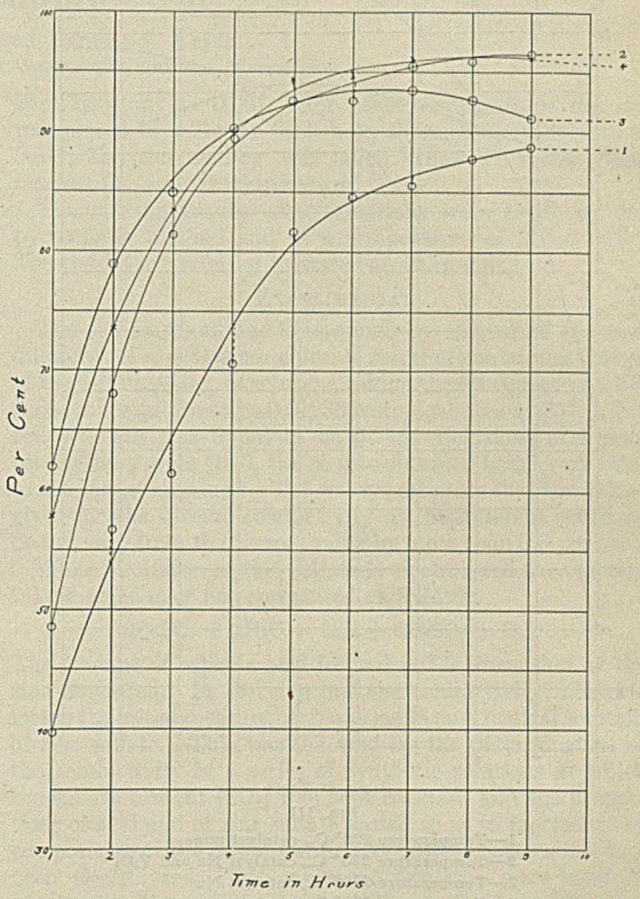

FIG. II

Temperature 220° C., 95% acid, 150% excess
1—Catalyst none 3—Catalyst V_2O_5
2—Catalyst Na 4—Catalyst Na and V_2O_5

TABLE 2

EXPT.	Average Temp. °C.	Catalyst	1st Hr.	2nd Hr.	3rd Hr.	4th Hr.	5th Hr.	6th Hr.	7th Hr.	8th Hr.	9th Hr.
			Yield of Disulfonic Acid in Per cent								
I*a*	221	....	39.6	56.6	61.3	70.5	81.6	84.5	85.5	87.7	89.0
II*a*	220	Na	48.5	68.0	81.3	89.5	....	92.6	95.7	96.0	96.7
III*a*	221	V_2O_5	61.9	78.8	84.8	89.7	92.6	....	93.5	92.8	91.2
IV*a*	221	Na and V_2O_5	57.9	73.4	83.3	90.1	94.3	94.5	96.1	....	96.4

Expt. I*a*, employing no catalyst, was carried out at an average temperature of 221°. A fairly consistent increase in the production of the di-acid took place throughout the 9 hrs.' heating. At the end of the first hour 39.6 per cent was found, while 98 per cent was shown to be present at the completion of the 9-hr. period.

In Expt. II*a*, 0.1 per cent of the element sodium was added in the form of carbonate and an average temperature of 220° was maintained. Here again the benefit derived from the use of sodium is readily seen, inasmuch as the curve holds well above the preceding one. This curve reveals the largest yield of the di-acid of any so far recorded—96.7 per cent at the end of 9 hrs.' heating. The influence of V_2O_5 at a temperature of 221° is shown by Curve 3, Fig. II. The amount of the catalyst added was 0.05 per cent. In contrast to the experiments at higher temperatures, the yields obtained are greater for the first 5 hrs. than when sodium is used, after which time the production lags somewhat behind

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[1] THIS JOURNAL, 12 (1920), 968.

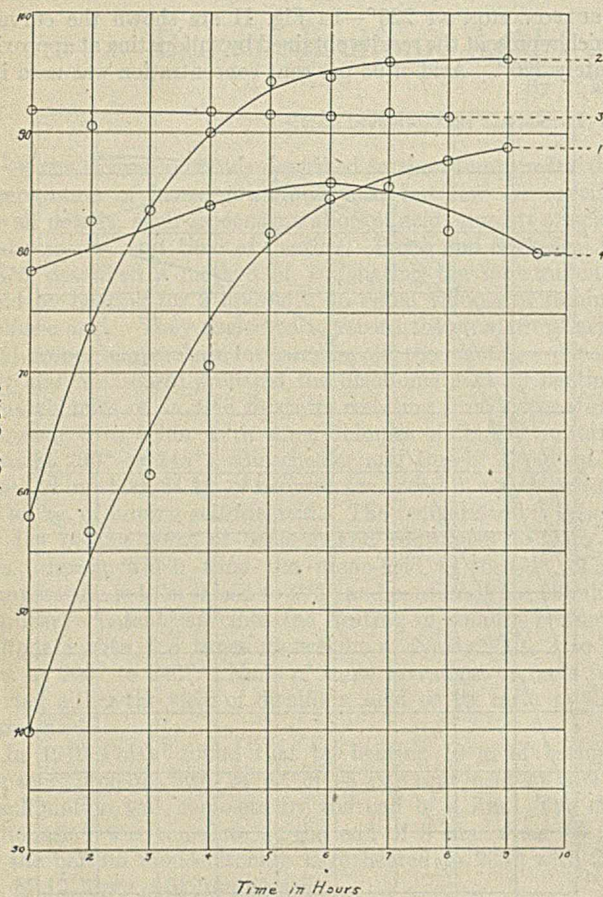

Fig. III

1—Temperature 220° C., catalyst none
2—Temperature 220° C., catalyst Na and V_2O_5
3—Temperature 250° C., catalyst Na
4—Temperature 250° C., catalyst none

that obtained with sodium. The results obtained by using both sodium and vanadium pentoxide at an average temperature of 221° are shown by Curve 4, Fig. II. Of the former 0.1 per cent was used, and of the latter 0.05 per cent was added. One hour's heating yielded 57.9 per cent of the diacid. Further heating gave a very consistent gain.

Curves 2 and 6, Fig. I, and 1 and 4, Fig. II, are brought together for a further comparison in Fig. III. These particular curves are chosen in order to represent clearly the best results with and without catalysts at both temperatures, 220° and 250°.

There is quite a noticeable drop in the amount of disulfonic acid found toward the end of some of the experiments. This is particularly true in those cases where the amount of excess acid is small, or a relatively high temperature is maintained, as shown by Curves 3, 4, and 9, Fig. I. This drop is probably due to the formation of sulfone compounds, such as benzenesulfonesulfonic acid, $C_6H_5SO_2C_6H_4SO_3H$, and benzenesulfonedisulfonic acid, $HSO_3C_6H_4SO_2C_6H_4SO_3H$.

The analytical results obtained where such compounds are present are, of course, in error in proportion to the amount of the sulfonesulfonic acid present. However, the actual amount of the disulfonic acid present is greater than the figures in such cases indicate. Evidence tending to prove the presence of such compounds was obtained by making sulfur determinations with the Parr calorimeter. More sulfur was found by this method than the barium method of analysis indicated was present.

Indication that a slightly greater amount of disulfonic acid is present at such stage in the sulfonation than the previous analytical results show is further given by fusion experiments made upon the purified sodium salts by Mr. Max Phillips of this laboratory. The methods of fusion and resorcinol determinations have already been described.[1] The optimum fusion conditions were followed. From the amount of resorcinol found in the fusion mixture the amount of disulfonate necessary for such a yield was calculated. This calculated amount was slightly greater than that found by determining the barium in a weighed sample of the dried salts.

Summary

The sulfonation of benzenemonosulfonic acid was carried out at temperatures approximating 220°, 250°, and 280°, using acid of 95 and 98 per cent concentration and varying in quantity from 50 to 700 per cent excess. The time variation was from 1 to 10 hrs.

The results obtained show that:

1—Of the temperatures tested, 250° is the most efficient, considering time and quantity of acid used.

2—Ninety-five per cent acid gives better results than 98 per cent.

3—A large excess of acid, such as 300 to 700 per cent, is unnecessary.

4—Sodium (introduced as the carbonate) and vanadium pentoxide act as catalyzers separately, but no particular advantage is gained by using both.

5—With sodium as a catalyst, heating for 1 hr. is sufficient.

American Field Service Fellowships for French Universities

Attention is again called to the fellowships offered by the Society for American Field Service Fellowships for French Universities. Applications for the 1922–23 awards must be made not later than January 1, 1922.

These fellowships, not to exceed twenty-five in number, are of the value of $200 and 10,000 francs. They are awarded for one year, and may be renewed for a second year. They are offered in various fields of science, art, and literature.

Applicants must be citizens of the United States, between twenty and thirty years of age, and must be graduates of a college requiring four years of study for a degree or of a professional school requiring three years of study for a degree, or, if not qualified in either of these ways, must be twenty-four years of age and have spent five years in an industrial establishment in work requiring technical skill. A practical knowledge of French is also essential.

Application blanks and complete information regarding the fellowships may be obtained from the Secretary, Dr. I. L. Kandel, 522 Fifth Ave., New York City.

Perkin Medal Award

The Perkin medalist for 1921 is Mr. William M. Burton, to whom the award is made in recognition of his work on the distillation of petroleum under pressure, resulting in the production of enormously large supplies of gasoline for fuel in internal combustion engines and of artificial asphalt which is largely used in the place of the natural product.

The medal will be presented at the meeting of the American Section, Society of Chemical Industry, at Rumford Hall, Chemists' Club, New York City, on January 13 1922.

Standard specifications for the testing and use of permissible explosives for use in mines, Bureau of Mines Schedule 17, are now before the American Engineering Standards Committee for consideration and approval as tentative American standard. These standards are the result of thirteen years' experience by the Bureau of Mines in testing and assisting manufacturers to develop explosives that offer the minimum hazard, when properly used, in gaseous and dusty mines. The final revision of these rules was made and approved as Schedule 17 on April 8, 1921.

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[1] This Journal, **12** (1920), 857.

The Electrical Conductivity of Solutions of Zinc Sulfate in the Presence of Sulfuric Acid[1]

By Herman V. Tartar and Harmon E. Keyes
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In the commercial production of metallic zinc by the electrolysis of zinc sulfate solutions, the energy relations of the zinc cell are naturally of importance, but many of the factors involved are not completely understood. The resistance of the electrolyte has an influence on the electrical power consumed and the amount of heat produced which must be dissipated by proper cooling facilities. The resistance varies with the temperature and the concentration of the zinc sulfate and of sulfuric acid. This variation in resistance is generally met with in practice to a very marked extent, since the process deals with an initial neutral solution of zinc sulfate, and sulfuric acid is formed during the electrolysis. Furthermore, the solution may undergo large temperature changes.

The present paper deals with an investigation of the conductivity of zinc sulfate solutions of the type used in certain typical plants, the observation being made over a temperature range of from 20° to 40° C. The object of the work was to determine the effect on conductivity of temperature, and acid and zinc concentration. Because of recent important work[2] on the deposition of zinc from strongly acid solutions (200 to 300 g. of free sulfuric acid per liter) and at high current densities, the work herein reported deals with both the higher and lower acid concentrations which may be used in commercial practice.

The writers believe that the results secured will possibly be of practical use in the zinc industry. There are few available data on this phase of electrolytic zinc. Furthermore, the calculation of the conductivity of such concentrated mixtures is, in the present state of our knowledge of the degree of ionization of the salt and of the acid in the presence of each other, practically impossible if accurate results are desired.

REAGENTS AND APPARATUS

Purified zinc sulfate was used throughout the experiments. It was made by dissolving "Baker's C. P." zinc oxide in pure sulfuric acid and distilled water, precipitating the metals electronegative to zinc with zinc dust and crystallizing out a portion of the zinc sulfate for use, the mother liquor being kept slightly acid to prevent the formation of basic salts. The zinc sulfate crystals were washed, dried by a suction filter, and assayed for zinc by titration with potassium ferrocyanide.

The sulfuric acid was "C. P. analyzed," the analysis showing no impurities to interfere.

The water used in making up the solutions had a specific conductivity 1.1×10^{-6} reciprocal ohms per cc.

The usual Kohlrausch method was followed in making the conductivity measurements. The set-up consisted of the customary Wheatstone bridge arrangement with slidewire of the drum type, standard resistances, a Leeds & Northrup alternating current generator operating at 1000 cycles per second and giving a nearly true sine-wave current, storage cells for furnishing current to the generator, and a suitable telephone receiver. The conductivity cell was of the cylindrical type, designed to conform approximately to the specifications of Washburn[3] for conductivity of the magnitude here involved. The electrodes were well platinized before use.

In making the measurements at 25° the conductivity cell was placed in a thermostat, the temperature of which was kept constant to 0.02°. For other temperatures the cell was placed in a Dewar flask with thermometer accurate to 0.01°, and the reading was taken when the solution had reached the desired temperature.

The specific gravity determinations were made by the pycnometer method and at a temperature of 25° ± 0.02°. The results are referred to water at 4° as unity.

EXPERIMENTAL

The cell constant was determined by measuring the conductivity of a potassium chloride solution containing 7.43 g. of the salt in 1000 g. of solution, taking the specific conductivity of this solution to be 0.01288 reciprocal ohm at 25°. The cell constant was found to be 6.245. Solutions of known conductivity were tried, the results obtained being very close to the accepted values. The writers estimate that the values given for the specific conductivity of the different solutions do not vary from the correct value by more than 0.5 per cent.

When a solution of zinc sulfate is electrolyzed the reaction taking place may be represented as follows:

$$2ZnSO_4 + 2H_2O = 2Zn + 2H_2SO_4 + O_2$$

The amount of sulfuric acid formed is 1.5 times that of the zinc deposited. In carrying out the conductivity measurements the initial measurement was made on a neutral solution of zinc sulfate. This was followed by the determination of the conductivity of a series of synthetic solutions in which the sulfate content (SO_4) was kept constant and the proportions of acid and of zinc sulfate varied so as to represent the composition of the initial solution at different stages if it had been electrolyzed. Two series of solutions were used; in one the starting point was a solution containing 200 g. of zinc (Zn) per liter and the other 100 g. per liter. The composition of each solution may be easily calculated from the formula:

$$\text{Solution} = ZnSO_4 \text{ required} + (\text{water in original solution} - \text{Zn deposited} \times 0.2755) + H_2SO_4 \text{ required}$$

Assays for sulfuric acid were made as final check on the accuracy of the preparation of the solutions. The values given for specific conductivity are expressed in reciprocal ohms (mhos) per cc. and are in each instance the average of four closely agreeing readings. These results may be converted into resistance in ohms per cu. in., which would be more useful in plant work, by simply dividing the factor 0.3937 by the given conductivity. The conductivity was determined at five temperatures, which cover the range met in actual practice. The composition and specific gravity of the solutions, the values for specific conductivity, and the temperature coefficients (which will be discussed later) are given in Table I. The data on composition are given in three ways; the figures for per cent by weight and grams per liter are included because both of these systems are in common use.

The temperature coefficient of conductivity (β) may be used in calculating the conductivity at any temperature from the expression:

$$\lambda_t = \lambda_{20°}\ (1 + \beta(t - 20))$$

where λ_t = conductivity at $t°$
$\lambda_{20°}$ = conductivity at 20°

In order to show more fully the effect of zinc sulfate and sulfuric acid on the conductivity, runs were made with several solutions, in which one of these substances was kept constant and the other varied. Data for specific conductance of

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[1] Received July 23, 1921.

[2] Tainton and Pring, U. S. Patents 1,059,233; 1,210,017; 1,247,179; "Tainton Process," *Eng. Min. J.*, **3** (1921), 341.

[3] *J. Am. Chem. Soc.*, **38** (1916), 2431.

TABLE I—COMPOSITION, SPECIFIC GRAVITY, SPECIFIC CONDUCTIVITY AND TEMPERATURE COEFFICIENTS OF CONDUCTANCE OF ZINC SULFATE-SULFURIC ACID SOLUTIONS

Sample No.	Zn Removed	Zn in New Soln.	H_2SO_4 Produced	H_2O G.	Per cent by Wt.		Sp. Gr. 25°/4°	G. per Liter Calculated		Assay H_2SO_4	Temp. Coefficient	Specific Conductance				
					Zn	H_2SO_4		Zn	H_2SO_4			20°	25°	30°	35°	40°
								SERIES I								
1	0	200	0	953.6	13.78	0	1.448	200.0	0	...	0.0329	0.0412	0.04755	0.0540	0.0611	0.0683
2	50	150	75.0	939.8	10.70	5.4	1.373	147.0	74.2	73.8	0.01815	0.1313	0.1439	0.1560	0.1676	0.1790
3	100	100	150.0	925.8	7.54	11.31	1.303	98.4	147.3	146.8	0.01442	0.2795	0.3013	0.3225	0.342	0.3601
4	120	80	180.0	920.5	6.14	13.82	1.275	78.4	176.3	175.5	0.01438	0.3533	0.3815	0.4067	0.4325	0.455
5	140	60	210.0	915.0	4.70	16.45	1.249	58.7	205.5	205.0	0.01432	0.437	0.472	0.503	0.5357	0.562
6	160	40	240.0	910.4	3.191	19.15	1.223	39.05	234.2	233.8	0.0145	0.527	0.567	0.607	0.644	0.680
7	170	30	255.0	906.8	2.42	20.55	1.211	29.33	249.0	248.5	0.0138	0.577	0.618	0.661	0.700	0.737
8	175	25	262.5	905.4	2.025	21.28	1.205	24.43	256.5	256.0	0.0139	0.598	0.640	0.682	0.726	0.764
9	185	15	277.5	902.7	1.228	22.70	1.1915	14.68	271.5	269.5	0.0140	0.644	0.692	0.737	0.781	0.824
10	190	10	285.0	901.3	0.8235	23.43	1.184	9.75	278.0	277.2	0.0139	0.668	0.722	0.765	0.812	0.854
11	197	3	295.5	899.4	0.249	24.50	1.175	2.928	288.0	286.5	0.0135	0.706	0.758	0.807	0.855	0.897
12	200	0	300.0	898.5	0	24.93	1.171	0	292.0	292.5	0.0134	0.723	0.775	0.825	0.874	0.917
								SERIES II								
1	0	100	0	984.8	8.11	0	1.232	100.0	0	...	0.0235	0.0500	0.0557	0.0615	0.0675	0.0735
2	20	80	30	979.3	6.635	2.485	1.201	79.6	29.85	...	0.0130	0.1055	0.1127	0.1197	0.1268	0.1329
3	40	60	60	973.8	5.075	5.075	1.172	59.5	59.5	...	0.00973	0.1783	0.1888	0.1980	0.2060	0.2130
4	60	40	90	968.3	3.456	7.775	1.143	39.51	89.0	...	0.00965	0.2712	0.2852	0.300	0.313	0.3235
5	70	30	105	965.5	2.620	9.18	1.129	29.6	103.6	...	0.01018	0.324	0.343	0.359	0.377	0.390
6	80	20	120	962.7	1.768	10.60	1.116	19.70	118.1	...	0.0108	0.381	0.403	0.424	0.445	0.463
7	100	0	150	957.3	0	13.56	1.089	0	147.7	...	0.0120	0.503	0.536	0.567	0.596	0.624

neutral zinc sulfate were secured to afford a basis for comparison. Since magnesium sulfate may be present in considerable quantity in the commercial solutions the effect of this salt on the conductivity of a mixture of sulfuric acid and zinc sulfate was determined.

The composition of the solutions and the specific conductance are given in Tables II, III, IV, and V. The results secured will perhaps be more readily understood from the curves given. The data in Table I are represented in Figs. 1, 2, 3, and 4. The data of Tables II, III, IV, and V are shown in Fig. 5.

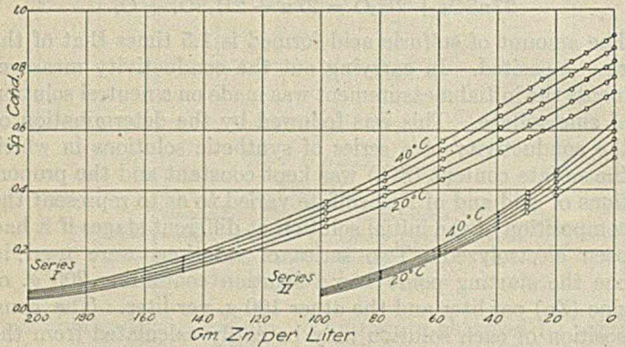


FIG. 1—CHANGE IN SPECIFIC CONDUCTIVITY OF ZINC SULFATE SOLUTIONS (INITIAL CONCENTRATIONS 100 AND 200 G. PER LITER) AS ZINC IS DEPOSITED ELECTROLYTICALLY AT DIFFERENT TEMPERATURES. CURVES INCLUDE VOLUME CHANGE

In view of the fact that it is common practice to add glue to the electrolyte to obtain better deposits of zinc, the specific conductivity of a sample which contained 230 g. of sulfuric acid and 50 g. of zinc (as zinc sulfate) per liter was determined before and after adding 0.02 and 0.09 g. of gelatin per liter. No change in the conductivity was detected.

TABLE II—EFFECT OF ZINC SULFATE ON SPECIFIC CONDUCTIVITY AT 25° OF SULFURIC ACID SOLUTION

SAMPLE	Zinc G. per Liter	Specific Conductivity
	H_2SO_4 = 230 g. per liter	
1	0	0.702
2	20	0.627
3	50	0.520
4	80	0.427
5	120	0.322
	H_2SO_4 = 150 g. per liter	
1	0	0.5358
2	60	0.383
3	100	0.301

TABLE III—EFFECT OF SULFURIC ACID ON SPECIFIC CONDUCTIVITY AT 25° OF ZINC SULFATE SOLUTION
(60 g. Zn per liter)

SAMPLE	H_2SO_4 G. per Liter	Specific Conductivity
1	0	0.0446
2	15	0.0784
3	25	0.1025
4	30	0.1145
5	50	0.1643
6	70	0.214
7	75	0.226
8	150	0.383
9	250	0.505

DISCUSSION OF RESULTS

In all cases the conductivity of the solutions rapidly increases with the sulfuric acid content. A neutral solution at 200 g. of zinc per liter would have its conductivity increased over fifteen times if the zinc were completely electrolyzed out of solution and an equivalent amount of sulfuric acid were formed. In practice it is not feasible to reduce the zinc content of the electrolyte below 20 g. per liter. When electrolyzed to 20 g. per liter zinc, a neutral solution of zinc sulfate containing 200 g. of zinc (Zn) per liter at 30° C. will have a specific conductivity of 0.71, while a neutral solution of 100 g. per liter of zinc when electrolyzed to the same zinc content will have a specific conductivity of 0.42.

In Fig. 5 is shown the increase in conductivity with acid strength for a solution containing 60 g. zinc per liter. The conductivity increases practically in proportion to the acid strength until about 125 g. per liter of acid is reached, when the rate of increase begins to fall off slightly. However, the highest acid strength shows the greatest conductivity.

TABLE IV—SPECIFIC CONDUCTIVITY OF NEUTRAL ZINC SULFATE SOLUTIONS AT 25°

SAMPLE	Zn G. per Liter	Specific Conductivity
1	10.0	0.01258
2	30.0	0.02865
3	60.0	0.0446
4	80.0	0.05115
5	100.0	0.0557
6	120.0	0.05685
7	150.0	0.0560
8	180.0	0.0515
9	200.0	0.04755

TABLE V—EFFECT OF MAGNESIUM SULFATE ON SPECIFIC CONDUCTIVITY AT 25° OF MIXTURE OF ZINC SULFATE AND SULFURIC ACID
(Zn = 55 g., and H_2SO_4 = 230 g. per liter)

SAMPLE	Mg. G. per Liter	Specific Conductivity
1	0	0.508
2	5	0.461
3	10	0.419
4	15	0.379

A solution carrying 117 g. per liter H_2SO_4 and 20 g. of zinc has a specific conductivity of 0.46 at 40° C., which would be a high temperature for regular operating work with the degree of electrolyte purification possible at the present time. However, a solution containing 263 g. H_2SO_4 per liter and 20 g. Zn has a specific conductivity of 0.615 at 20°, a temperature lower than that generally employed. This shows that strong acid electrolytes, at a moderately low temperature, have a much higher conductivity than weak acid solutions even when raised to a temperature higher than is generally considered permissible. The curves in Fig. 5 show that with the neutral solution the point of maximum conductivity

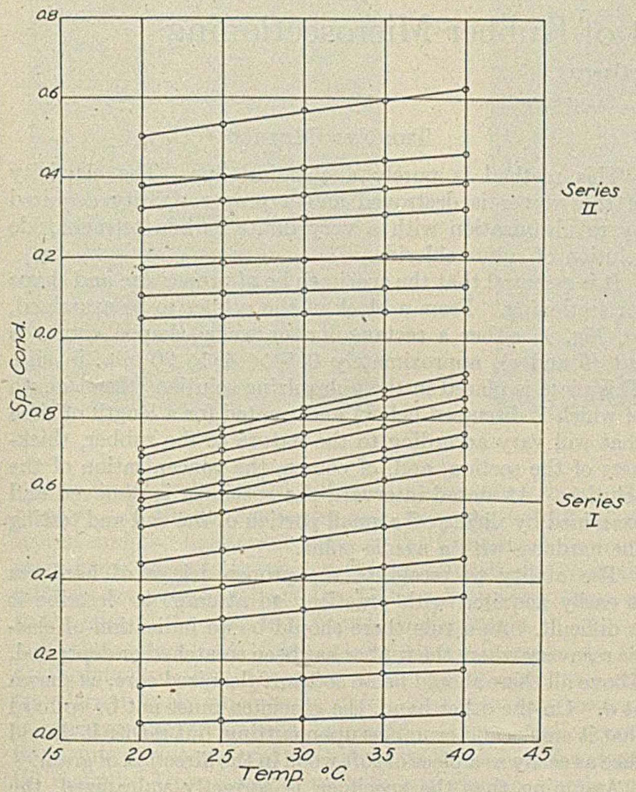
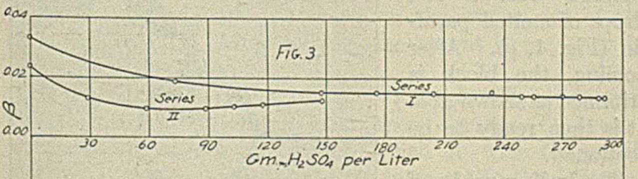


FIG. 2—EFFECT OF TEMPERATURE ON THE SPECIFIC CONDUCTIVITY OF SOLUTIONS OF SERIES I AND II

is reached at 120 g. zinc per liter, and that the conductivity of strong sulfuric acid solutions is diminished by zinc sulfate. This increase in resistance, due to the addition of zinc, is more marked the stronger the acid and is probably caused by the increased sulfate (SO_4), which may lower the concentration of the hydrogen ion by repressing the ionization or by forming complex compounds with the acid. If this be true, the presence of other metallic sulfates should produce a similar effect. The data in Table V, which are shown graphically in Fig. 5, substantiate this statement and show that the resistance of the given solution is increased 25 per cent by adding 15 g. of magnesium per liter in the form of sulfate.



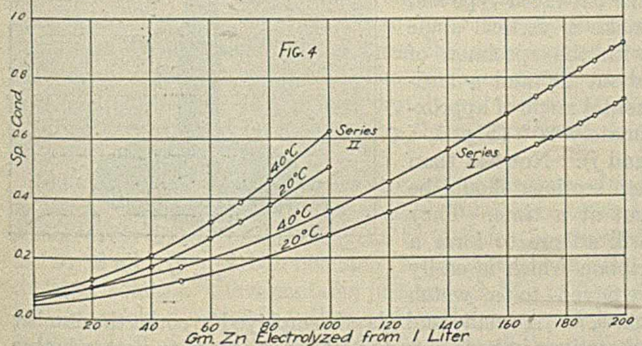


FIG. 3—VARIATION OF TEMPERATURE COEFFICIENTS OF SPECIFIC CONDUCTIVITY OF SOLUTIONS OF SERIES I AND II

FIG. 4—CHANGE IN SPECIFIC CONDUCTIVITY OF ZINC SULFATE SOLUTIONS OF SERIES I AND II AT 20° AND 40° WITH INCREASE OF ZINC DEPOSITED (THE ACID STRENGTHS COINCIDE). CURVES INDEPENDENT OF VOLUME CHANGE

The two series in Table I are plotted in Fig. 4, with the acid strength coinciding. The solutions with lower zinc concentrations have higher conductivity than those of the same acid strength and higher zinc content. However, as shown in Fig. 1, when the same data are plotted with the zinc concentrations coinciding, the higher acid strengths give the greater conductivity, and therefore the highest conductivity is ultimately reached with the solutions which originally contained the greatest concentration of zinc.

From the results in Table I it is evident that a volume change accompanies the electrolysis, there being an actual *increase* in volume notwithstanding a loss of zinc and oxygen. Theoretically, when 200 g. of zinc have been deposited from a liter the resulting solution assays only 292 g. per liter of H_2SO_4 instead of 300. When 100 g. of zinc are electrolyzed out of solution the gain in volume is about 1.5 per cent. This is a fact not generally considered in plant control.

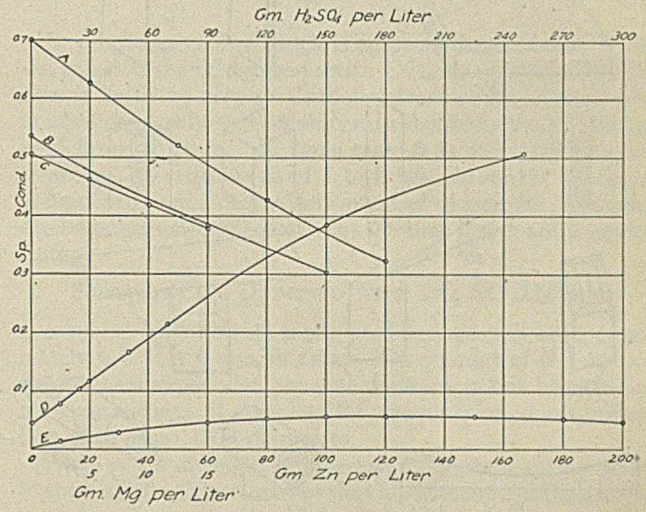


FIG. 5—INFLUENCE ON SPECIFIC CONDUCTIVITY OF VARIATIONS OF SULFURIC ACID OR METAL SULFATE CONTENT

A—H_2SO_4, 230 g. per liter, varying $ZnSO_4$
B—H_2SO_4, 150 g. per liter, varying $ZnSO_4$
C—$ZnSO_4$ and H_2SO_4, 55 g. Zn and 230 g. H_2SO_4 per liter, varying $MgSO_4$
D—$ZnSO_4$, 60 g. Zn per liter, varying H_2SO_4
E—Neutral $ZnSO_4$

The increase of conductivity with temperature which is given in Fig. 2 is a nearly linear function. The temperature coefficients vary with the strength of the original neutral solution and the extent of electrolysis (Fig. 3).

SUMMARY

1—The conductivity of zinc sulfate electrolyte greatly increases with sulfuric acid concentration.

2—The conductivity of sulfuric acid is diminished by the addition of zinc sulfate. Adding magnesium sulfate to a strongly acid zinc sulfate solution causes an additional decrease in conductivity.

3—The temperature coefficients of conductivity vary and are a function of the acid and zinc concentration.

4—The addition of 0.02 to 0.1 g. of gelatin per liter has no influence on the conductivity.

5—The conductivity of an acid zinc sulfate solution appears to be due largely to hydrogen ion, and lowering of the hydrogen-ion concentration by the addition of metal sulfates decreases the conductivity.

6—The deposition of zinc is accompanied by an increase in volume, amounting to 1.5 per cent for each 100 g. of zinc deposited.

Recent Development in the Art of Rubber Microsectioning[1]

By Henry Green

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There has lately appeared an article[2] by Messrs. Depew and Ruby in which the authors point out the desirability of studying the nature and dispersion of compounded pigments in rubber microsections.

Their method of preparing the sample for sectioning, by freezing with carbon dioxide and liquid air, entails certain disadvantages which are difficult or quite impossible to overcome. Chief among these are the annoyances encountered in obtaining, transporting, and keeping liquid air. In addition, the method usually necessitates the use of large amounts of carbon dioxide, before a satisfactory section can be secured. The main drawback is met in the comparatively high temperature of the knife. As the blade passes over the specimen, the heat it (the blade) contains is partly transferred to the frozen rubber causing it to thaw, with a consequent change in volume, thus making it impossible to regulate the thickness of section. This fact is particularly objectionable when it is desired to obtain the thin sections required for the examination of rubber containing high percentages of gas black. Briefly, the method fails economically, both in respect to expense and time.

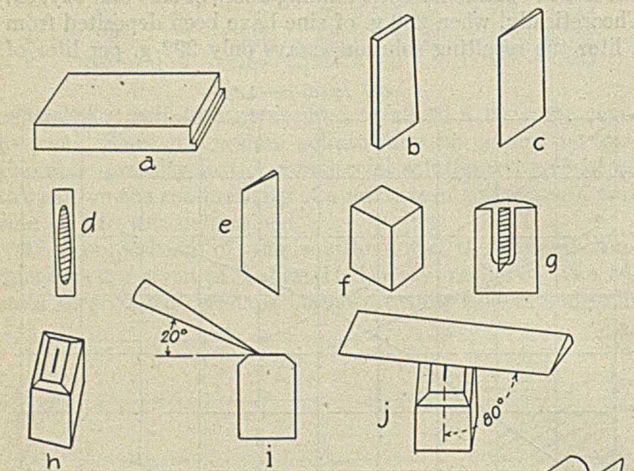

Fig. 1

After stating the objections to the freezing method it would hardly be fair to omit emphasizing its chief virtue, *i. e.*, the fact that the specimen is not chemically prepared, and therefore a possibility of destroying the rubber structure or influencing the dispersion of the pigment is eliminated. For this reason, alone, it is not desirable to abandon entirely the idea of employing the freezing method at times.

The New Method

This method is purely a chemical one. The elasticity of the rubber is destroyed and a proper rigidity acquired by revulcanization with a very dilute carbon tetrachloride solution of sulfur chloride.

It is essential that the specimen be of proper size and shape for sectioning. From a block of the rubber to be examined, (*a*, Fig. 1) either a rectangular or wedge-shaped corner is cut (*b* and *c*), approximately 0.5 × 4 × 20 mm. in size. This piece is placed in the vulcanizing solution (the strength of which is discussed below) and treated for a length of time that will vary according to the nature of the rubber, thickness of the section, and, of course, the concentration of the solution. At stated intervals, the specimen is removed and examined by slicing off a small portion of the end and testing the hardness with a needle point.

The ability to recognize the proper degree of hardness is easily acquired with practice; to attempt to describe it is difficult. As a rule there should be no indication of elastic recovery where the rubber has been scratched or depressed. Above all there should be no soft unvulcanized core, as shown at *d*. On the other hand, the specimen must not be so hard that it cracks and crumbles upon cutting, but rather it should slice as easily as a piece of soft wood in the direction of grain.

Assuming that the specimen is correctly vulcanized, the next step is to allow it to become thoroughly dry (preferably by vacuum treatment) and then to sharpen it at one end, as at *e*, simply for convenience in inserting it in the paraffin mounting block. This block, *f*, is rectangular in shape and roughly 15 × 15 × 30 mm. It is clamped in a vise and a hot nail or other convenient instrument pushed into its upper end to a depth of about 18 mm., to produce a cavity in which the specimen is placed. The pointed end *e* must be pressed firmly into the paraffin and the face of the block covered with a few drops of melted paraffin (Fig. 1, *g*). After cooling, the block is trimmed as shown at *h*. It is then ready to be sectioned.

The knife must be of the flat-faced type and make a vertical angle with the specimen of about 20° and a horizontal angle of approximately 80° (Fig. 1, *i* and *j*). Not less than ten sections should be cut at a time. They will adhere to form a ribbon which is easily removed to a watch glass, *k*. A small hand glass is employed to count the number of sections imbedded in the ribbon in order to note whether the microtome has "skipped" or not. In case it has, it is then impossible to ascertain the thickness of the section from the microtome setting.

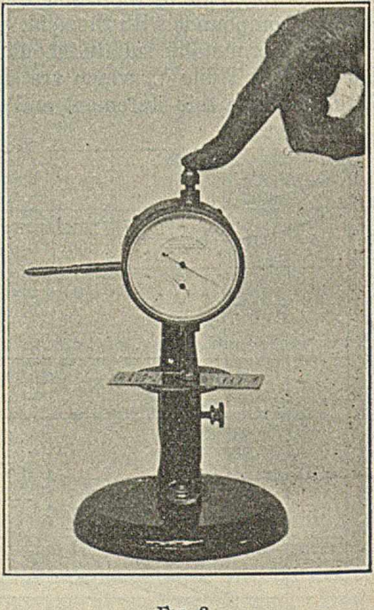

Fig. 2

The paraffin adhering to the microsection is now removed with a few cc. of toluene. The specimens, upon examination,

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

[2] "Some Microsections Cut from Vulcanized Rubber Articles," This Journal, 12 (1920), 1156.

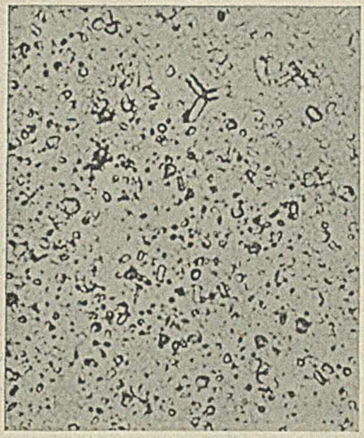

FIG. 3

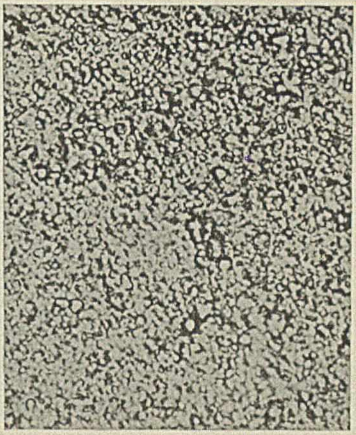

FIG. 4

FIG. 5

will be found to be curled either in the manner shown at *l* or at *m*. If the former is the case, they will be difficult to uncurl and the horizontal angle of the knife must be made more acute so as to prevent this form of curling. Next the sections are removed from the toluene by sliding them up to the edge of the glass with the aid of the needle.

If the sections are thick (3–5μ) they will probably become detached from the glass upon drying and are easily transferred to the microscope slide. The mounting medium is piperine (never Canada balsam).[1] A few small crystal fragments of this material are placed on the slide and warmed till melted. Upon cooling, piperine will remain plastic and sticky for some time. While in this condition, the section is placed on its surface and covered with a glass (Fig. 1, *n*). Upon alternately warming and pressing on the cover glass the excess of piperine is gradually squeezed out.

The specimen is next examined with a low power microscope. If it is found to be badly wrinkled, as shown at *o*, or to contain objectionable air bubbles, the slide is transferred to a hot plate and heated for a minute or so till the piperine is quite fluid. While in this state it is necessary to apply a comparatively high pressure in order to remove the air bubbles and at the same time to flatten the section as much as possible. The author has found a thickness gage convenient for this purpose. The slide is placed on the stage and pressure applied with the finger on the upper end of the plunger (Fig. 2). After cooling, the mount is ready to be labeled and examined.

If the section is quite thin (0.5–1.5μ) it will not become detached from the watch glass upon drying. In such a case it is sometimes possible to detach it with the needle point. If this fails it is necessary to resort to the following method: First melt the piperine on the microscope cover glass, instead of the slide. Invert it so that the drop will hang downward. Upon solidification press the drop against the section, as shown at *p*, Fig. 1. The specimen may become slightly damaged by this process but it will adhere to the piperine and can now be mounted by the method previously described.

Reference has been made to the strength of the vulcanizing solution. This will vary with the kind of rubber to be treated. A zinc oxide tread, for instance, can be sufficiently prepared in 5 to 10 min. in a carbon bisulfide (N. B., not carbon tetrachloride) solution which contains just enough SCl to impart to it an easily discernible yellow tint, perhaps several drops in 50 cc. of solution. If this is found to be too weak the strength may be increased or the specimen sliced thinner. The best concentration is in all cases quickly and easily found by trial.

In preparing rubber which is compounded with gas black, the solution should be made with CCl_4, as otherwise brittleness is liable to ensue. Carbon tetrachloride solution acts much more slowly and consequently should be made stronger —15 drops to 50 cc. In some cases it is necessary to allow treatment to continue from 1 to 3 hrs. before the specimen is hardened completely. Any number of samples, however, can be prepared together so that the time lost is not a serious factor.

SOME RESULTS OBTAINED WITH THE SCl METHOD

A rubber microsection made as described will be approximately 0.5 × 4.0 mm. in area. On account of the minute size of the compounded pigment particles it has been found most convenient to employ for examination a magnification of at least 1500 diameters.

While a microsection of this size may seem rather small to show all the characteristics that a particular rubber sample possesses, in reality it will be found amply large enough. If the field of the microscope were so extended that it could give a single view of the entire section it would appear (at 1500 diam.) to be a strip, in round numbers, 3 ft. by 20 ft. in area.

Sections prepared by the sulfur chloride method possess beautiful transparency and uniformity in thickness. They are practically ideal for visual examination where it is always possible, by varying the fine adjustment, to bring any part of the mount (and at any depth) into focus, hence the slight lack of flatness, which these sections often have, is not objectionable.

A section which is not perfectly flat is a difficult one to handle from a photomicrographic viewpoint; however, most specimens contain areas that are sufficiently free from this defect so as to enable one to obtain fairly satisfactory photomicrographs.

Fig. 3 is a zinc oxide tread. No difficulty is experienced in obtaining good sections of rubber compounded with normal amounts of this material. On account of its transparency these sections may be cut quite thick (3–5μ).

Fig. 4 is a specially prepared sample containing 100 volumes of rubber to 100 volumes of zinc oxide. Even with this high percentage of oxide the pigment particles are uniformly distributed, showing absence of aggregation. The section was not difficult to make.

No photomicrograph can do justice to the sections presented in Figs. 5 and 6. The former shows lampblack, always existing in rubber flocculated into small groups with clear water-white spaces between. The individual particles are not discernible as they are never found dispersed. A great deal of the detail in this section cannot be seen in the

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[1] In a rubber section mounted in balsam, zinc oxide becomes quite invisible, excepting the largest particles, which are always readily seen.

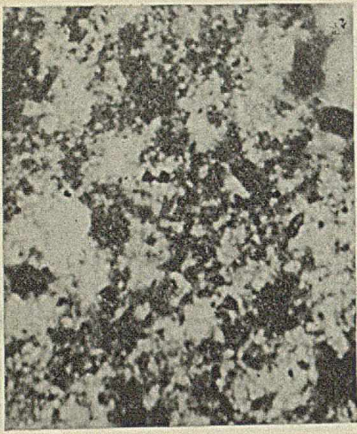

FIG. 6

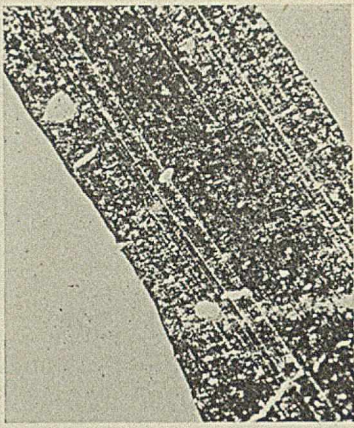

FIG. 7

FIG. 8

photomicrograph. Fig. 6 is rubber compounded with gas black. This black is found much better distributed than the former, though one inexperienced in work of this nature might easily infer otherwise from a comparison of the photomicrographs. Here again (in Fig. 6) much of the detail observable with visual examination is lost in the attempt to reproduce it photomicrographically. As a matter of fact, a more difficult subject than rubber containing normal amounts of gas black cannot be found in the entire field of photomicroscopy. There is no difficulty whatever in readily distinguishing between a rubber compounded with lampblack and another containing gas black, upon microscopic examination.

Fig. 7 shows a tread containing gas black and clay. The magnification is but 67.5 diameters. The clay is best examined between crossed nicols where it shows extinction and interference colors. Fig. 8 is the same sample magnified 1500 diameters in order to observe the gas black, individual particles of which can be seen along the edge of the clay particle.

Frequently, rubber compounded with gas black will be found to contain innumerable pocket-like spaces absolutely devoid of pigment particles. Fig. 9 shows a section of this kind. So far it has been impossible to determine whether these spaces are empty or contain a substance which the gas black particles are unable to penetrate. Fig. 10 is a rough torn edge of a similar section showing a sponge-like structure, due to these pockets.

Growth of crystalline substance in rubber is an interesting procedure to study. Fig. 11 is a section containing crystallized para toner. This substance is first dissolved in melted paraffin in which the rubber is soaked before sectioning. The sample was not treated with sulfur dioxide, no pigment being present to interfere with the transparency, hence a thick section (100–200μ) could be used. The paraffin itself will produce sufficient rigidity to make possible the cutting of these abnormally thick sections.

The microsection was next washed with toluene to remove the paraffin and then dried and mounted in glycerol. If such a mount is examined immediately it will be found that the para toner has crystallized and if the process of crystallization is to be studied, solution must first be obtained by warming the slide. The rubber will act as a liquid solvent and cause complete solution of the toner. When recrystallization commences it can be studied microscopically, using a low power objective. The material sends out branches apparently with perfect freedom just as though it were suspended in a liquid medium instead of a solid one.

FIG. 9

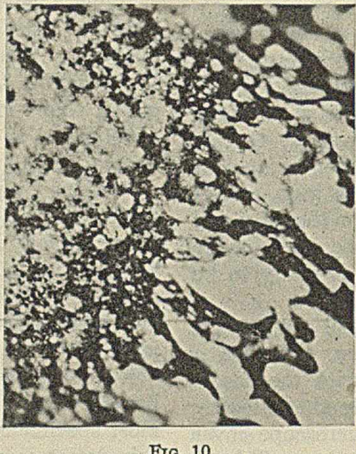

FIG. 10

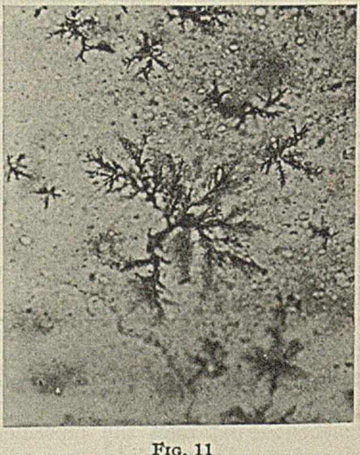

FIG. 11

In conclusion the author wishes to state that he has constantly borne in mind, while preparing rubber microsections by the sulfur chloride method, that the rubber is given a chemical treatment that might possibly produce effects not present in the untreated original specimen. In order to ascertain if undesirable alterations had appeared it was necessary to make comparisons with specimens prepared by the freezing method. Wherever it was possible to do this the results given by the two methods were found to be identical.

ACKNOWLEDGMENT

The author wishes to acknowledge his indebtedness to Mr. Howard M. Cyr for valuable aid received from him during the preparation of this paper.

The Relation between Coefficient of Vulcanization and Mechanical Properties of Vulcanized Rubber[1]

By O. de Vries

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Our scientific knowledge of rubber and its vulcanization is still so deficient that even a number of the most fundamental points on which rubber testing should be based are insufficiently cleared up. For instance, it still forms a point of discussion whether the mechanical properties or the coefficient of vulcanization are the most important in judging the state of cure of vulcanized rubber. Some argue that the mechanical properties of the vulcanized article are the only ones that interest the buyer, while he is indifferent as to how much sulfur has combined with the rubber to reach the degree of elasticity and strength that suits his purpose. Others point out that the mechanical properties are not constant in a colloid like rubber, while the coefficient of vulcanization is not changed by mechanical treatment and is also independent of aging—or at least nearly so at ordinary temperatures—so that in general the coefficient is a better indication of the state of cure to which the rubber was originally brought.

Discussion on this point may well rest till sufficient experimental material has been gathered to clear it up definitely; elsewhere[2] we have summarized the present situation as follows: "As the determination of the coefficient of vulcanization means a considerable amount of additional work, and gives no actual gain in the routine of our testing of estate samples, we have not included it in our regular tests," and further, "When one wants to gain as complete an insight as possible into the properties of so complicated a substance as vulcanized rubber, both coefficient of vulcanization and mechanical properties have to be taken into consideration."

Effect of Added Accelerators on Coefficient of Vulcanization

From the latter standpoint, one of the first subjects for further research is the difference in coefficient of vulcanization for different types of rubber, cured to the same mechanical properties (position of the stress-strain curve). It has been remarked by many investigators that, when curing to a fixed cure as judged by the stress-strain curve, the coefficient of vulcanization may vary over a rather wide range. An especially striking example has been recently published by D. F. Cranor,[3] who found that the coefficient for a given curve was influenced largely by the addition of accelerators. For instance, when cured to a certain curve, mixtures with and without an accelerator gave the following coefficients:

Sample	Time of Cure Minutes	Coefficient of Vulcanization Per cent
Original smoked sheet.....	198	4.9
Same, with 0.5 per cent hexamethylenetetramine.	35	1.8
Same, with 0.5 per cent dimethylamine derivative....................	2.4	0.9

Effect of Natural Accelerators

The accelerators increase the rate of cure enormously, and at the same time the coefficient for given mechanical properties decreases markedly. This may be explained in several ways. The organic accelerators may have a stronger accelerating effect on the processes that alter the mechanical properties than on the combining of the rubber with sulfur. Or, the very short time during which the rubber is exposed to the high temperature of vulcanization may avoid the disintegrating effect of heat (which is opposite to the stiffening effect of vulcanization). Be this as it may, if powerful organic accelerators give such a marked difference in the coefficient of vulcanization for a fixed curve that the question arises, what may be the effect of the so-called natural accelerators in plantation rubber? These accelerators are either constituents of the latex as it comes from the tree, or decomposition products formed from the non-rubber constituents during preparation. They are supposed to be amines or amino acids, and are undoubtedly very powerful accelerators, since they give a marked increase in rate of cure although present in the rubber in only very small quantities.

Ordinary plantation rubber, tested in pure rubber-sulfur mixtures, indeed shows the phenomenon of differences in coefficient of vulcanization for fixed mechanical properties, but the variation is by no means as large as in the above example.

A. van Rossem[1] studied this variation for a large amount of statistical material. For our purpose his results may be summarized as follows: Taking as the basis of comparison a stress-strain curve for which the average coefficient of vulcanization is 5.0, out of a number of samples of ordinary first quality crepe or smoked sheet, 50 per cent will not show a larger variation in coefficient of vulcanization than 0.25. For the bulk of plantation rubber, therefore, the relation between stress-strain curve and coefficient is rather close.

Effect of Time of Cure on Coefficient of Vulcanization

The question further arises, which types of plantation rubber show a coefficient higher than the normal, and which show a lower one?

B. J. Eaton and F. W. F. Day[2] found the coefficient of vulcanization for standard mechanical properties (their optimum curve) to be:

	Standard Time of Cure Hours	Coefficient of Vulcanization Per cent
Ordinary crepe............	3.25	4.1 -4.5
Crepe from matured rubber	1.25	4.65-5.1

Matured rubber is prepared by keeping the coagulum in the wet state for some time. A decomposition then sets in, and the protein decomposition products cause an increased rate of cure. Eaton and Day therefore find an increase in coefficient, the more natural accelerator the rubber contains. H. P. Stevens[3] for three samples of rubber finds the following figures for the coefficient of vulcanization at fixed positions of the curve.

	Position of Curve			
	Load in Kg./Sq. Mm. at 1000 Per cent Length			
Sample	700	900	1100	1300
	Coefficient of Vulcanization			
Smoked sheet................	1.8	2.1	2.4	2.7
Crepe.......................	2.3	2.65	2.95	3.25
Crepe from matured rubber....	2.4	2.85	3.1	3.2
	Time of Cure (Min.)			
Smoked sheet................	77	90	103	116
Crepe.......................	113	132	150	168
Crepe from matured rubber....	57	70	77	81

Up to a coefficient of 3.1 the rapid-curing matured rubber shows higher figures than the ordinary crepe, as in Eaton and Day's experiments. The sample of smoked sheet, though

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[1] Received May 2, 1921.

[2] O de Vries, "Estate Rubber, Its Preparation, Properties and Testing," 1920, 489, 531.

[3] *India Rubber World*, **61**, 137; *India Rubber J.*, **58**, 1199. For further examples see A. van Rossem (*Comm. Gov. Inst. Delft*, **1917**, 213; D. F. Twiss and S. A. Brazier, *J. Soc. Chem. Ind.*, **39** (1920), 125; H. P. Herens, *India Rubber World*, **62**, 720.

[1] Comm. Gov. Inst. for Advising the Rubber Trade (Delft), V, 164.

[2] *J. Soc. Chem. Ind.*, **36** (1917), 1116.

[3] *Ibid.*, **37** (1918), 280*t*.

curing more quickly than the crepe, shows throughout a much lower coefficient for the same curves.

The author gathered some material to make a further study of this point. In the first place, we may mention some samples of ordinary crepe of different rate of cure. These gave:

Sample	Standard Time of Cure Minutes	Coefficient of Vulcanization
660	85	5.1
602	90	5.0
1897	94	5.0
1667	115	4.4
1204	120	4.75
1602	122.5	4.4

The coefficient of vulcanization is determined for our standard state of cure,[1] for which the length at a load of 1.30 kg. per sq. mm. is 990 per cent. The more quickly curing crepes, which contain more of the natural accelerators, show a higher coefficient of vulcanization in accordance with the results of Eaton and Day and of Stevens.

Some specially prepared samples of abnormal composition gave the following figures:

No.	Sample	Description	Standard Time of Cure Minutes	Coefficient of Vulcanization
1	2467	Matured rubber	30	4.9
2	1883	Latex evaporated to dryness	65	5.1
3	2459 W	Ball smoked after Brazilian method	70	5.25
4	2365 DW	Ball smoked after Brazilian method	70	5.1
5	2365 BW	Ball smoked after Brazilian method	80	5.15
6	2494 A	First clot in partial coagulation	85	5.3
7	2494 B	Rest after partial coagulation	115	4.35
8	2494 C	Ordinary coagulation	115	4.65

The first sample is matured rubber (slab rubber) and may be classed among those with the greatest rate of cure as yet known. Like all matured rubber it contains natural accelerators formed by decomposition of proteins, but less non-rubber constituents than ordinary crepe, as part of the serum substances has been decomposed and escaped in gaseous form (loss in weight about 1.5 per cent). The coefficient of vulcanization is higher than normal.

The second sample is also quick curing; it contains all the latex constituents, being prepared by rapid evaporation of latex by hot air (Kerbosch process);[2] no maturation or decomposition of serum substances has taken place. The coefficient of vulcanization is higher than normal, as in the foregoing case.

Samples 3 to 5 have been prepared after the Brazilian method (smoked balls), Sample 3 by a native smallholder and Samples 4 and 5 as part of the output of a large European estate. The samples were 0.5 to 1 yr. old when tested, and showed the ordinary rather rapid rate of cure of balls of that age.[3] Smoked balls retain somewhat more serum substances than ordinary crepe and smoked sheet, but they contain by no means all latex constituents, as a large amount of serum drips out during and after preparation. Maturation takes place slowly in the balls, bringing the time of cure from 100 to 50 min. in the course of 2 yrs.[4] The coefficient of vulcanization for this type is higher than the average and nearly the same as in former cases.

Sample 6 is prepared from the first clot obtained in partial coagulation. Such rubber contains more by-substances than ordinary crepe; it cures more quickly (though no maturation has taken place). The properties of Samples 6 to 8 were:[5]

No.	Moisture	Ash	Aqueous Extract	Acetone Extract	Viscosity	Tensile Strength	Slope
6	1.40	0.35	0.51	4.2	35	1.40	33
7	0.64	0.17	0.13	2.7	23	1.39	36
8	0.93	0.28	0.11	3.2	30	1.46	36

In this case also the coefficient of vulcanization is higher than normal for the more quickly curing sample.

Though these four types of quick-curing rubber are prepared in totally different manners, and show large differences in composition (both in amount of serum substances and in accelerator formed by maturation), the excess in coefficient of vulcanization is nearly the same in all cases.

Plantation rubber therefore seems to show a higher coefficient of vulcanization than normal when it is quick curing, independent of whether the quicker cure is caused by unchanged latex constituents or by decomposition products formed by maturation. The few exceptions to this rule deserve further study.

In future investigations of this kind it will be interesting to push the analysis further by determining not only the total combined sulfur in the ordinary way, but by differentiating between the sulfur bound by the rubber and by the nonrubber constituents as proposed by W. J. Kelly.[1] Perhaps a difference as between Samples 7 and 8 might be cleared up in this way.

SUMMARY

The natural accelerator or accelerators in rubber cause an increase in coefficient of vulcanization for fixed mechanical properties, which amounts to about 0.5 for all types of quick-curing rubber, independent of their composition. The natural accelerators therefore act in exactly the opposite way to the artificial accelerators about which data are now available.

The effect of the natural accelerators on the coefficient for a fixed curve seems to be much less pronounced than in the case of those artificial accelerators.

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[1] See "Estate Rubber, Its Preparation, Properties and Testing," 463, 542.

[2] "Estate Rubber," p. 436.

[3] *Ibid.*, pp. 422–431.

[4] *Ibid.*, pp. 422-431

[5] Compare *Arch. Rubbercultuur*, **1** (1917), 185; *J. Soc Chem. Ind.*, **38** (1919), 92; *India Rubber J.*, **57** (1919), 1164; "Estate Rubber," p. 389.

[1] This Journal, **12** (1920), 875.

Organization of the Natural Resources Production Department of the Chamber of Commerce of the United States is just being perfected. The department is preparing a very active program in an effort to render constructive service to the raw material industries, supplementary to the work of the various trade associations. It is believed that great assistance can be rendered to the industries and to the public by conducting a campaign of education intended to enlighten the public on the vital problems of natural resource activities. The following advisory committee has been appointed: C. S. Keith, Central Coal & Coke Co., Kansas City, chairman; J. H. Ross, Exchange Supply Co., Winter Haven, Fla.; J. E. Spurr, *Engineering and Mining Journal*, New York City; Christy Payne, Peoples & Hope Natural Gas Cos., New York; E. T. Meredith, former Secretary of Agriculture, Des Moines, Iowa; Sidney J. Jennings, United States Smelting, Mining & Refining Co., Boston, Mass.; R. V. Norris, mining engineer, Wilkes-Barre, Pa.; Van H. Manning, American Petroleum Institute, New York; and William H. Davis, Mid-Continent Oil & Gas Association, Bartlesville, Okla.

Canadian pulp and paper exports for September reached a value of $9,457,027, a decline of $7,033,665 as compared with September 1920 and an increase of $51,635 over August 1921. Exports of newsprint for the month amounted to 1,224,136 cwt., compared with 1,212,225 in September 1920. Countries of destination were:

	Paper	Pulp
United Kingdom	$ 116,591	$1,221,245
United States	5,249,548	2,175,937
Other countries	408,468	285,328

Comparative figures for the first six months of the fiscal year show:

	Paper	Pulp	Total
1921	$33,379,508	$15,804,159	$49,183,667
1920	43,025,764	44,217,712	87,243,476
1919	27,119,246	16,626,726	43,745,972

Pul[illegible] exported to the United States for the first six months of the year were as follows:

1919	515,444 cords	$5,089,693
1920	653,856	7,803,332
1921	421,388	5,546,785

The Properties and Action of Enzymes in Relation to Leather Manufacture[1]

By **Joseph Turney Wood**

TURNEY BROTHERS, LTD., NOTTINGHAM, ENGLAND

THE SOAKING PROCESS

Enzymes occur in and influence almost all the operations of tanning from the moment that the skin is flayed until it is dried out in the form of leather. The fresh skin contains a number of enzymes about which very little is known and other enzymes are soon formed by bacteria. We shall not consider these in any detail, as we may assume that the raw skin has been properly preserved after flaying and before coming into the hands of the tanner, but in the soaking process we meet with enzymes secreted by a variety of species of bacteria. Most of these bacteria liquefy gelatin by means of the proteolytic enzymes which they secrete, and consequently they attack the skin. So far as the writer knows, the bacteria of the soaks have not been specially studied except by Andreasch,[2] who isolated a number of species of bacteria from the soaks. He identified the following:

B. fluorescens liquefaciens (Flügge)
B. megaterium (de Bary)
B. subtilis
B. mesentericus vulgatus
B. mesentericus fuscus
B. mycoides (Flügge)
B. liquidus (Frankland)
B. gasoformans (Eisenberg)
White bacillus (Maschek)
Proteus vulgaris
Proteus mirabilis
B. butyricus (Hueppe)
White streptococcus (Maschek)
Worm shaped streptococcus (Maschek)
Gray coccus (Maschek)

All these may be classed as putrefactive organisms, and they secrete a variety of enzymes, some of which act energetically on the hide substance. Fig. 1 shows a typical plate culture on gelatin of a soak used for softening dry sheep skin, in which no chemicals have been used. The development of the colonies had to be stopped by the application of formalin vapor before many of the species had time to develop; otherwise the whole plate would have been liquefied. In view of the fact that the enzymes in the soaks are nearly all derived from bacteria, it is evident that the soaking should be carried out under antiseptic conditions as far as possible.

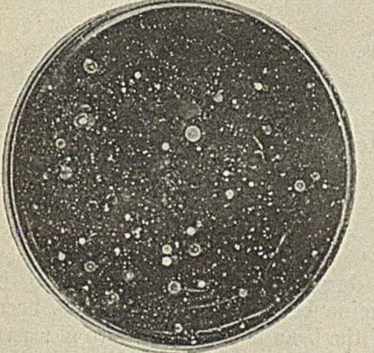

FIG. 1—TYPICAL PLATE CULTURE ON GELATIN OF SOAK USED FOR SOFTENING DRY SHEEP SKINS

Rideal and Orchard[3] examined the action of *B. fluorescens liquefaciens* on gelatin to which was added 10 per cent of Pasteur's solution to serve as nutrient medium. The gelatin was completely liquefied in 3.5 days. It was shown that the liquefaction of gelatin was due to an enzyme, or enzymes, secreted by the bacteria. The liquefied gelatin was alkaline and had a slight putrefactive odor, but contained no hydrogen sulfide. A notable feature was the small amount of ammonia and volatile bases produced; only 0.2 g. of ammonia per 100 cc. were produced even after 16 days' incubation. The liquefaction of gelatin by pancreatic trypsin takes place with much greater rapidity; 0.2 mg. of the enzyme preparation will liquefy 5 cc. of 4 per cent gelatin in 30 min. at 39°.

THE LIME LIQUORS

In a lime liquor through which skins have passed, there are enzymes present. The writer is inclined to believe that some of these are from the skin itself, at least when fresh market skins are worked, as, for example, the tissue enzymes, but nothing definite is known of these. Bacteria, however, develop in the limes. *B. prodigiosus* and *Micrococcus flavus liquefaciens*, both of which are known to produce proteolytic enzymes, have been identified. These enzymes decompose the dissolved skin substance into gelatones (gelatin-peptones) and eventually into amino acids, caproic acid, and ammonia. It is very probable that the enzymes in the limes act in the same way as the enzymes in the sweating process of unhairing, but in the limes the process stops short of putrefaction, whereas in the sweating stove it may go on until the skin is run on the grain.

THE BATING PROCESS

The investigation of the action of the bates or puers has proved of great interest and has resulted in the use of scientific methods depending on the use of commercial enzymes in leather manufacture. The object of bating or puering is to render the skins, and the resulting leather, soft and supple. Skins which have undergone the liming process must be thoroughly freed from lime before going into the tan liquors, and for light and soft leather they must be reduced or "brought down" so that the elasticity or resilience of the skin fibers is got rid of, and the skin when tanned can be stretched without springing back. In the case of the old manure bates for light leathers, this is done by passing the skin through a bate or puer composed of an infusion of dogs' dung in water at a temperature of 35° to 40° until the desired result is obtained. This condition is known to the workman by the feel of the skin. The process has been in use from the very earliest times, but until comparatively recently no explanation of the action of the dung bates was satisfactory.

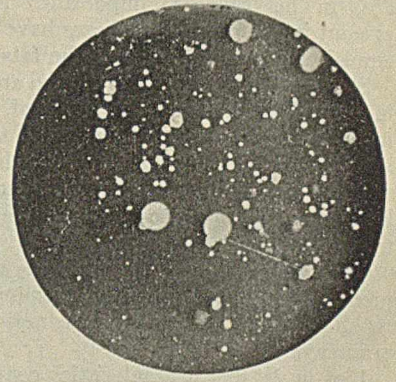

FIG. 2—TYPICAL PLATE CULTURE ON GELATIN OF PURE LIQUOR

Thirty years ago, when the author commenced the investigation of the action of the dung bate in the manufacture of light leathers, he came to the conclusion that a great part of the bating effect was due to the action of proteolytic enzymes on the skin in conjunction with ammonium salts present in the bate. The latter not only combined with the lime remaining in the skin, but also acted as activators for the enzymes. Numerous experiments were made on skins both in the presence of growing bacteria and of the products of the bacteria, precipitated by alcohol, and it was found that when suitable ammonium salts were present the bating action in both cases was similar.

There is little doubt that every variety of enzyme, hydrolyzing, oxidizing, ammoniacal, etc., is produced by bacteria. The production of enzymes by bacteria was observed by Wortmann in 1882, and Fermi and others have investigated the enzymes of the bacteria which liquefy gelatin. Since the

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

[2] *Gerber*, 1895-6.

[3] *Analyst*, October 1897.

bacteria in the bate produced these enzymes, the first idea was to use them in practice in a scientific way. In conjunction with Prof. H. Becker, we manufactured a bacterial bate "Erodin," which the writer believes was the first attempt to apply the use of pure cultures of bacteria in the leather industry. The bacterium used was a variety of *B. coli* isolated from dog dung. Harden[1] has shown that this bacterium produces at least three enzymes.

An investigation of the enzymes contained in dog dung showed that five different enzymes were present:[2]

1—A peptic enzyme resembling stomach pepsin.
2—A tryptic enzyme, or enzymes, resembling pancreatic trypsin.
3—A rennin (coagulating enzyme).
4—An amylolytic enzyme.
5—A lipase.

In view of the fact that the bate solution is alkaline, it seemed pretty certain that trypsin must be the principal enzyme acting, and it is this enzyme which has been applied practically in the manufacture of artificial bates.

It must be clearly understood that, although the enzymes and ammonium compounds are the chief bodies acting on the skin in the dung bate, they are not the only bodies taking part in the process. As the writer has shown, there are many other bodies in the dung which act in a way at present not understood. Among these the fats, soaps, and phosphates are, in his opinion, important. Among other enzymes present in the dung, the lipases have a considerable effect in emulsifying and hydrolyzing the fats.

Skins which have been overlimed are bated more effectively in a dung bate than in an artificial, enzyme bate, and this must be due to some constituents in the dung bate which are absent from the enzyme bate. It has further been shown that excessive liming so alters the chemical constitution of the hyaline membrane as to render it capable of being attacked by trypsin.

Rosenthal[3] states that elastin is digested in the bating process; and more recently Seymour-Jones has been able to show that the elastin is contained principally in the grain layer.

Elastin is the characteristic constituent of the elastin fibers which remain after treating the skin with boiling water, caustic alkali, dilute hydrochloric acid, alcohol, and ether. It is of pale yellow color and is insoluble in any menstruum which does not act on it chemically. When boiled with strong hydrochloric acid and stannous chloride, leucine (30 to 40 per cent) and a small quantity of tyrosin (0.25 per cent) are found among the products of its decomposition, together with ammonia, glycine, and aminovalerianic acid, but not aspartic or glutamic acid. This behavior distinguishes elastin from both proteids and gelatin, since the former yield aspartic and glutamic acids but no glycine, while gelatin never yields a trace of tyrosin. Elastin is digested by the body enzymes. It is allied to the fibroin of silk and spider web.

Quite independently J. A. Wilson[4] has shown definitely that the elastin of the skin is removed by the tryptic enzymes of the bate. In the unbated skin the elastin fibers are fairly dense in the grain layer. As the bating proceeds, they gradually disappear, and at the end of 24 hrs. the grain is quite free from elastin. In skin delimed with ammonium chloride only, the elastin was left apparently unaltered. Wilson concludes that the mechanism of bating consists of two distinct parts: (1) reducing the limed skin to a condition of minimum swelling, and (2) digesting the elastin fibers present in the outer layers of the skin. It may be added that Mr. Seymour-Jones considers the so-called hyaline layer to be really the deepest layer of the epithelium, and proposes to call it the grain membrane, as being more in harmony with the nomenclature of the leather industry. In light leather manufacture it is what is called a "flywing" and yields practically no gelatin on boiling, whereas the split flesh is wholly transformed into gelatin.

Although the elastin is completely removed from the skins bated by trypsin for a sufficiently long time, about 24 hrs., in practice the bating is not continued to this point, but is carried on for only about 2 to 6 hrs. The elastin is only partly removed in this time, but the skins make good leather. The writer believes that it is not necessary, or even desirable, for the whole of the elastin to be removed or dissolved in order to let the skin down, but that it is sufficient for the elastic fibers to be broken up or weakened, in order that the desired suppleness may be obtained.

There still remain many unsolved problems in the bating process; these are being pursued with vigor, and the writer looks forward confidently to the time when we shall be able to bate any kind of skin by means of artificial bates suitable to the particular leather required.

DRENCHING

In the manufacture of many kinds of light leathers, skins are drenched after bating. This process usually consists in placing the skins in a mixture of bran and water (5 to 10 g. per liter) at a temperature of 30° to 35°. This ferments vigorously for 18 to 24 hrs., with evolution of a considerable quantity of gas and the formation of weak organic acids. In a drench taken in actual work, the gases had the following composition:

	Per cent
Carbon dioxide	25.2
Hydrogen sulfide	Trace
Oxygen	2.5
Hydrogen	46.7
Nitrogen	26.0

The acids produced per liter were:

	Gram
Formic	0.0306
Acetic	0.2042
Butyric	0.0134
Lactic	0.7907

Of other bodies formed during drenching, the quantity is insignificant, trimethylamine being the chief. It has been shown that the starch of the bran is converted into glucoses and dextrin by the action of an amylolytic enzyme, cerealin, allied to diastase. This enzyme was discovered by Mege Mouries.[1] It resembles the diastase of translocation described by Brown and Morris[2] in their work on the germination of grass seeds. It transforms starch into dextrin and glucose, whereas ordinary malt diastase transforms starch into dextrin and maltose. The action of cerealin is much slower than that of diastase. Dr. W. H. Wilcox and the author found that in 12 hrs. at 40° about one-half the starch is transformed. With malt extract, the whole of the starch disappears in about 2 hrs. The glucoses are then fermented by bacteria (*Bacillus furfuris*) with the formation of the organic acids above mentioned. The principal acid produced is lactic; the acetic acid is produced directly from the glucoses without any preliminary alcoholic fermentation by yeasts.

The mode of action of the drench on the skins is as follows:

1—Solution of the last traces of lime not removed by the bate and the subsequent swelling action of the organic acids on the skin fibers. The acids also dissolve a small amount of skin substance.

2—Distension and floating of the skins by the gases produced by the fermentation.

3—Mechanical absorption of dirt by the particles of bran or flour in the drench.

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[1] *Chem. World*, **1912**, 403.

[2] *J. Soc. Chem. Ind.*, **31** (1912), 1105.

[3] "Biochemical Studies of Skin," *J. Am. Leather Chem. Assoc.*, **11** (1916), 463.

[4] THIS JOURNAL, **12** (1920), 1087.

[1] *Compt. rend.*, **37** (1853), 351; **38** (1854), 505; **43** (1856), 1122; **48** (1859), 431; **50** (1860), 467.

[2] *J. Chem. Soc.*, **57** (1890), 458.

It will thus be seen that the action of enzymes in the drench is an indirect one.

Tan Liquors

In the tan liquors changes go on which are brought about by enzymes; some of these are secreted by molds and yeasts and others are present in the plants from which the tanning materials are extracted. Unfortunately very little is known about these enzymes, but attention should be called to the work of Fernbach[1] in France, who prepared an enzyme which he called tannase from the mold *Aspergillus niger*, obtained from gall nuts. He cultivated the mold in Raulin's liquid, using tannin in place of the sugar. The product was macerated in water, the maceration concentrated at a low temperature *in vacuo*, the liquid precipitated by alcohol, and the precipitate treated exactly as in Lintner's method for the preparation of amylase. The gray powder thus obtained, when dissolved in water, acted rapidly on tannin at 50°, converting it into gallic acid. The solution of tannase filtered through a Chamberland filter into a sterilized solution of tannin acted just as effectively, proving that the action was due to an enzyme and not to a fermentation through the agency of organized cells.

H. Poltevin[1] prepared a solution of tannase by a process similar to that of Fernbach, but independently of him. Along with the gallic acid formed there is also a variable amount of glucose in the case of commercial tannins, but he considers these commercial tannins as mixtures. From a purified tannin he obtained gallic acid corresponding to 98.5 per cent of the tannin. The fact that tannase also hydrolyzes phenyl and methyl salicylates lends support to Schiff's formula for tannin, $C_6H_2(OH)_3.COO.C_6H_2(OH)_2.COOH$. In nature tannin is often accompanied by gallic acid. No doubt the latter is formed by the action of tannase, which Poltevin found to exist in sumac leaves, and which no doubt occurs in other substances containing tannin.

A Critical Study of Bating[2,3]

By John Arthur Wilson and Guido Daub

Laboratories of A. F. Gallun & Sons Co., Milwaukee, Wisconsin

In an earlier paper[4] it was shown that the mechanism of bating limed skins in the tannery by means of pancreatin and ammonium chloride consists of two distinct parts: reducing the skins to a condition of minimum swelling, and digesting the elastin fibers which are present only in the outer layers of the skin. The progress of this digestion was shown by means of photomicrographs of cross sections of the skin taken at intervals during bating. The examination of more than 200 sections under the microscope failed to reveal any other function of the bating process, even when a great variety of stains was employed on the sections. It therefore would appear that the primary function of bating is the removal of elastin, since the skins may be brought to a condition of minimum swelling simply by regulating the hydrogen-ion concentration of the solution with which they are in contact and, furthermore, this condition is only a temporary one, while the removal of elastin is permanent. The work described in this paper was confined to a study of the removal of elastin from calfskin and its effects.

Preparation of Skin for Examination

The most reliable method we know for studying the progress of bating is by means of the microscope. The per cent of elastin removed by any treatment is estimated by observing under the microscope cross sections of the samples taken before and after the treatment. For this purpose the sections must be suitably prepared, and the following procedure has been found quite satisfactory. Strips of the sample, about 2 in. × 0.5 in., are dehydrated with alcohol and soaked successively in (1) a mixture of equal volumes of alcohol and xylene, (2) a mixture of 1 volume of melted phenol to 3 of xylene, (3) pure xylene, and (4) melted paraffin, after which they are imbedded in paraffin and sectioned at 40μ. The sections are then stained either by means of Weigert's stain as described by Gage[5] or by the following method which the writers have found convenient: The section is washed on a slide with xylene, then with the alcohol-xylene mixture, and finally with pure alcohol. The whole slide is covered with alcohol saturated with Bismarck brown and kept over night in an airtight jar containing alcohol. Next day the section is rinsed with alcohol, alcohol-xylene, phenol-xylene, and finally with pure xylene. A drop of Canada balsam and a cover glass are then put over the section, which is now ready for examination and may be kept indefinitely for record.

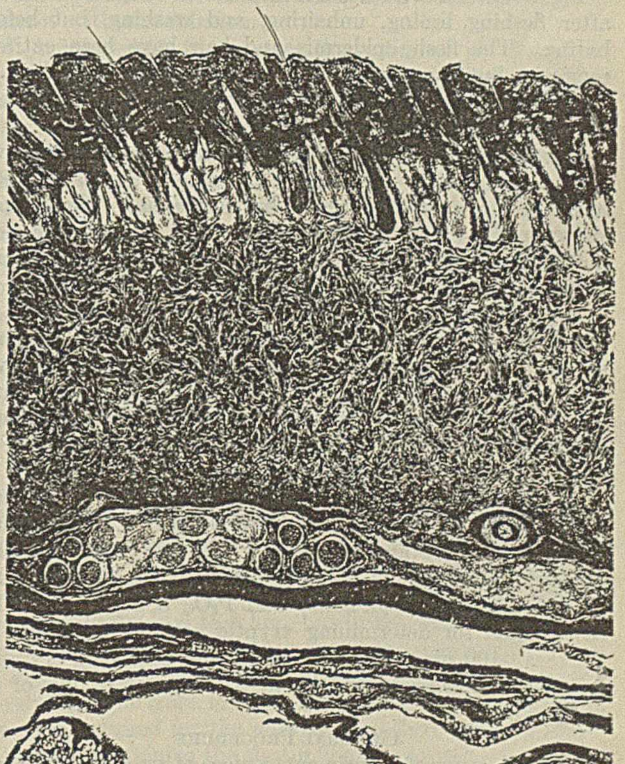

Fig. 1—Cross Section of Skin of Young Heifer Calf. Magnification, 25 Diameters

Fig. 1 is a photomicrograph of a cross section of the skin of a healthy young heifer calf. A strip from the butt was taken an hour after the death of the animal and fixed in Erlicki's fluid. A section was stained first with Weigert's stain and then with an alcoholic solution of picro-red. It was photo-

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[1] *Compt. rend.*, **26** (1848), 1214; *J. Soc. Chem. Ind.*, **20** (1901), 137.

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

[3] Received August 3, 1921.

[4] This Journal, **12** (1920), 1087.

[5] "The Microscope," **1917**, 355.

[1] *Compt. rend.*, **26** (1848), 1215; *J. Soc. Chem. Ind.*, **20** (1901), 137.

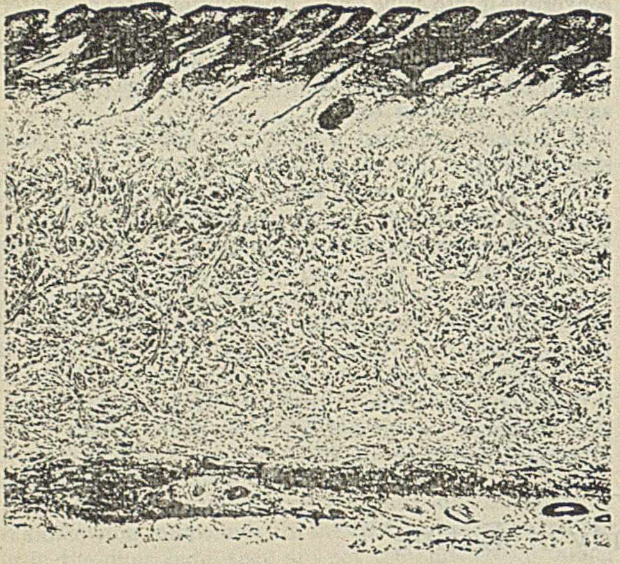

Fig. 2—Cross Section of Calfskin Taken after Fleshing, Liming, Unhairing, and Washing, before Bating. Magnification, 25 Diameters

graphed through a combination of Wratten filters B-2 (green) and E-2 (orange). The elastin fibers show as a dark layer about 0.4 mm. deep between the epidermis and hair roots. Other layers of elastin fibers are visible in the flesh, supporting the nerve bundles and fat cells.

Fig. 2 represents a section from the butt of a calfskin taken after fleshing, liming, unhairing, and washing, but before bating. The flesh, epidermis, and hair have been entirely removed, but the elastin fibers are still intact and show as dark layers near the upper and lower surfaces of the skin. The main body of the skin contains no elastin.

Fig. 3 represents a section from the same skin as that shown in Fig. 2, but was taken after bating. The elastin fibers have been completely digested by pancreatin. The sections shown in Figs. 2 and 3 were prepared and stained with alcoholic Bismarck brown exactly as described above. They were photographed through a Wratten filter H (blue-green).

Estimates of the per cent of elastin removed were made on the basis of removal from the grain layer only. In some cases all of the elastin was removed from the grain layer before half of it was removed from the flesh layer. Since the shaving operation removes practically all of the flesh elastin, its removal in bating is of little importance.

Materials Used

The chemicals employed were the ordinary C. P. variety. The enzyme was a commercial sample of U. S. P. pancreatin which showed by analysis: water, 6.3 per cent; insoluble matter, 40.0 per cent; ash, 6.8 per cent; N, 11.0 per cent; Cl, 1.7 per cent; SO_3, none; and P_2O_5, 3.5 per cent. By the method for determining tryptic activity described by Thomas,[1] 100 mg. of the sample acting upon 1 g. of casein in 100 cc. of solution for 1 hr. at 40° digested 64 mg. of nitrogen.

General Procedure

For each series of experiments a piece of limed and unhaired calfskin was cut into strips about 2 in. × 0.5 in. and thoroughly washed. There is a small, but appreciable, difference in time required for complete removal of elastin from skins of different thickness and for this reason great care was exercised in selecting all strips for any one series from the same part of the same skin, so as to have them all as nearly identical as possible. Each strip was put into 500 cc. of liquor, a volume large enough to prevent the skin from seriously altering the concentration of the liquor. The liquors were put into dark brown bottles to shield them from the light and were kept in a large Freas thermostat for the stated lengths of time at 40° ± 0.01°, the optimum temperature for most enzyme actions.[1]

Every liquor contained 0.02 mole per liter of added phosphoric acid to act as a buffer in addition to the enzyme and the KOH required to give the desired hydrogen-ion concentration. The hydrogen-ion concentration of each liquor was determined both before and after the digestion period by means of Hildebrand electrodes and a Leeds and Northrup potentiometer, excepting where it was proved by previous test that the results obtained by the Clark and Lubs series of indicators were sufficiently accurate. Except for the more strongly acid and alkaline solutions, the change in pH value during digestion was practically negligible.

As a rule, a preliminary series covering a very wide range was run, followed by a second series covering only the active range of the enzyme. A third series was usually run as a check.

Effect of Hydrogen-Ion Concentration

It is well known that the hydrogen-ion concentration is an important factor in determining the rate of digestion by enzymes. Using 0.1 g. of pancreatin per liter and digesting for 24 hrs., the writers obtained complete removal of elastin from the skin only between the pH values 7.5 and 8.5. A portion of the pancreatin was put into a collodion sac and dialyzed against running tap water in a dark room for 16 hrs. and used in a duplicate series in such quantity as to represent 0.1 g. per liter of the original pancreatin. The results were the same as those obtained with undialyzed enzyme. A series was then run in which the concentration of pancreatin was increased to 1.0 g. per liter. Complete removal of elastin was obtained between the pH values 5.5 and 8.5. The results of the two series, which are shown in Fig. 4, were carefully checked to insure their accuracy. The per cent of total elastin removed is plotted against the pH value of the solution taken after digestion and cooling to 25°.

The peculiar relation of the curves to each other is significant. They nearly coincide at all pH values above 7.5, but at 6.0 the stronger solution is still at its optimum activity, while the weaker one has apparently entirely lost

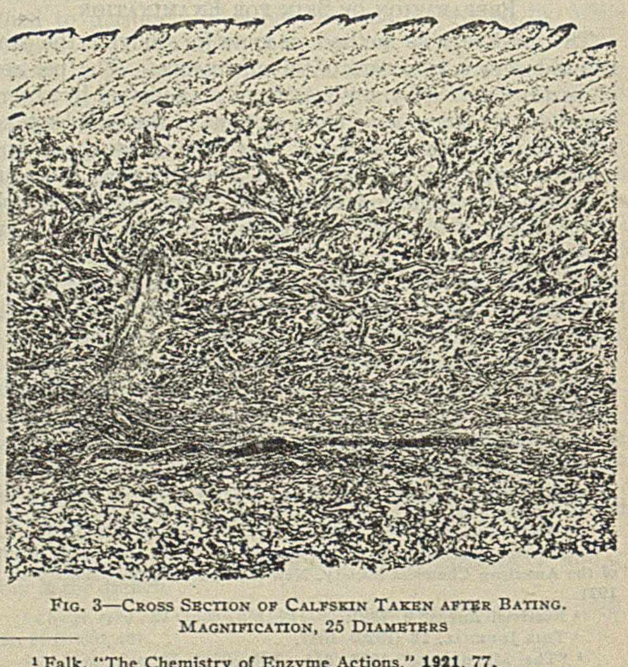

Fig. 3—Cross Section of Calfskin Taken after Bating. Magnification, 25 Diameters

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[1] J. Am. Leather Chem. Assoc., **15** (1920), 221.

[1] Falk, "The Chemistry of Enzyme Actions," **1921**, 77.

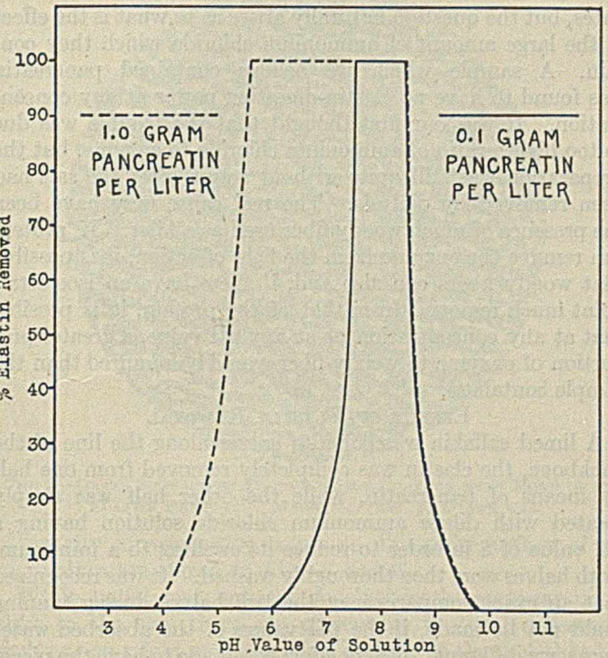

Fig. 4—Removal of Elastin Fibers from Limed Calfskin as a Function of Hydrogen-Ion Concentration. Time of Digestion 24 Hrs.; Temperature 40° C.

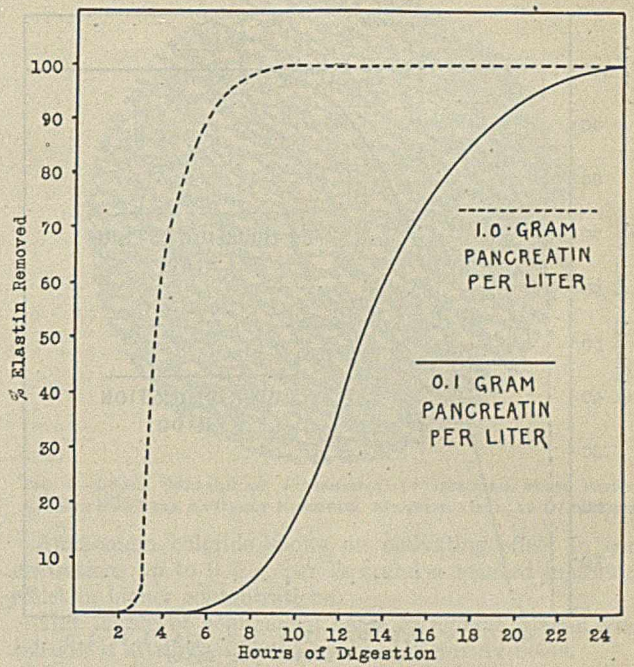

Fig. 5—Removal of Elastin Fibers from Limed Calfskin as a Function of Time of Digestion. Temperature 40°; pH Value 7.6

its elastin-digesting powers. When an enzyme has been found to have different optimum pH values with different substrates, it has been supposed that the effect of the hydrogen-ion concentration upon the substrate has been the determining factor. But here we have the same enzyme and the same substrate, with a change in the optimum range due merely to a change in concentration of the enzyme.

An explanation is suggested by the recent work of Northrop,[1] who has shown that the activity of an enzyme solution is not necessarily a function of the apparent total enzyme concentration, but that a portion of the enzyme may be inactivated by combining with peptone or other foreign matter. He has pointed out further that the extent of the formation of addition compounds between protein and enzyme depends upon the concentration of protein ion, which is in turn a function of the hydrogen-ion concentration. If some protein other than elastin is responsible for the inactivation of a portion of the enzyme, we should expect such action to be a minimum at the isoelectric point of this protein.

After bating, the strips of calfskin were all carefully examined for the "bated feel," which apparently bears no relation to elastin removal, but corresponds to a condition of minimum swelling of the skin. The only strips passing this test were those from liquors having pH values between 6.10 and 9.80, suggesting that the isoelectric point of at least one of the skin proteins lies between these points. The average of these is 8, which is also the midpoint of the optimum range for the more dilute enzyme solution.

The following explanation is therefore not an improbable one: At a pH value of about 8, practically all of the enzyme is left free to attack the elastin, but as the pH value is decreased and the concentration of protein ion correspondingly increased, more and more enzyme is removed from the field of action by combining with it. In the weaker solution at pH = 6.0 practically all of the enzyme is in combination with this protein, whereas in the stronger solution the excess of enzyme is still sufficient to digest elastin. In dealing with the effect of hydrogen-ion concentration upon enzyme action, it is evidently important to know the effect of the hydrogen-ion concentration upon each substance in contact with the solution.

It is interesting to compare the optimum pH values for tryptic digestion found by other investigators:[1] for albumose Michaelis and Davidsohn[2] found 7.7, for casein Sherman and Neun[3] found 8.3, while Long and Hull[4] found 5.5 to 6.3, and for fibrin Long and Hull[4] found 7.5 to 8.3. The total range of 5.5 to 8.3 corresponds closely to the range found by the present authors, 5.5 to 8.5, for complete removal of elastin by the more concentrated enzyme solution.

At pH values less than 3.0 there was a marked destruction of the collagen fibers, possibly due to acid hydrolysis, and the strips were much swollen and rubbery, but no removal of elastin could be detected.

Effect of Time of Digestion

Two series of solutions were prepared, one in which the concentration of enzyme was 0.1 g. per liter and the other in which it was 1.0. All members of both series were otherwise identical. The pH value of each liquor was brought to 7.6 and this did not change during digestion. Each strip of calfskin was kept in a separate bottle. The bottles were removed from the thermostat at fixed intervals during 24 hrs.

Complete removal of the elastin was effected by the stronger enzyme solution in 6 to 8 hrs., but in the weaker solution 24 hrs. were required. The progress of the digestion is shown in Fig. 5. The time required to start digestion, 2 hrs. for the stronger and 5 hrs. for the weaker solution, was apparently the time required for the enzyme to diffuse into the region of the skin containing the elastin fibers. As will be seen from Fig. 2, these begin about 0.1 mm. below the grain surface.

Effect of Concentration of Enzyme

Two identical series of solutions were prepared in which the individual members differed only in concentration of pancreatin. The pH value was fixed at 7.6. One series was kept in the thermostat for 5 hrs. and the other for 24 hrs. The results are shown in Fig. 6 and furnish a study in economy.

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[1] *J. Gen. Physiol.*, **2** (1920), 471; **3**, 211.

[1] Cf. Falk, *Loc. cit.*, p. 66.

[2] *Biochem. Z.*, **36** (1911), 280.

[3] *J. Am. Chem. Soc.*, **38** (1916), 2203; **40** (1918), 1138.

[4] *Ibid.*, **39** (1917), 1051.

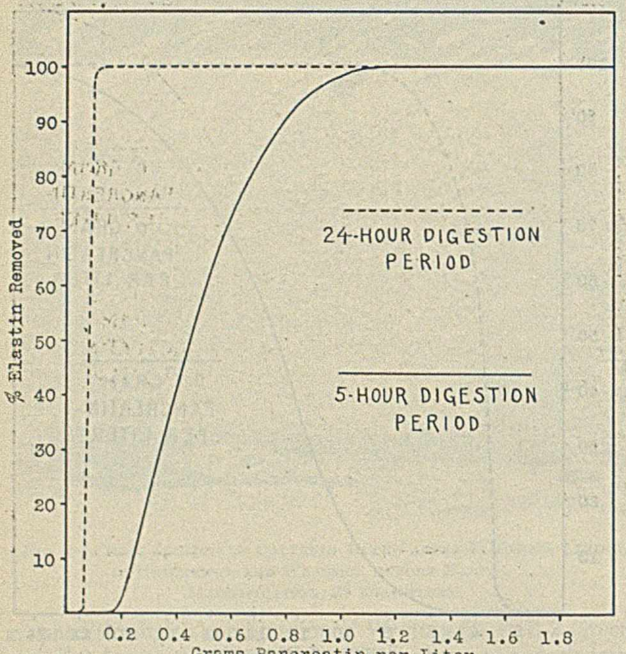

Fig. 6—Removal of Elastin Fibers from Limed Calfskin as a Function of Concentration of Enzyme. Temperature 40°; pH Value 7.6

Complete removal of elastin is effected by 0.1 g. of pancreatin in 24 hrs. or by 1.1 g. in 5 hrs.

Effect of Concentration of Ammonium Chloride

A study of bating would not be complete if it did not include the effect of ammonium chloride, one of the most abundant constituents of commercial bating materials. Aside from its use as a filler, it has been assumed to be beneficial in removing lime from the skins and tending to maintain a slight alkalinity favorable to tryptic digestion.

In this experiment two series of solutions were prepared in which the concentration of enzyme was 0.1 and 1.0 g. per liter, respectively. To each successive member of each series increasing amounts of ammonium chloride were added and the pH values of all members brought to 7.6. The time of digestion was 24 hrs. (Fig. 7).

In working with very dilute enzyme solutions, a distinct activating effect was noted upon the addition of 0.5 g. per liter of ammonium chloride, while larger amounts showed an inhibitory effect. With thin calfskin the activating effect was not detectable with the solution containing 0.1 g. per liter of enzyme after a 24-hr. digestion period, because all of the elastin was removed without adding any ammonium chloride. In order to show the activating effect in these experiments, strips from heavier skins were used, which require a somewhat longer time for complete removal of elastin under fixed conditions. The activating effect of 0.5 g. of ammonium chloride per liter and the inhibitory effect of greater concentrations are very marked. It is also interesting to note that the effect of ammonium chloride can be entirely overcome by a sufficient excess of enzyme.

This behavior of ammonium chloride is interesting in view of the finding of Thomas[1] that potassium bromide in concentrations of 0.0 to 0.1 mole per liter has an inhibitory effect upon the action of malt amylase, but in greater concentration has an activating effect.

At concentrations greater than 50 g. per liter the ammonium chloride exerted a destructive action upon the collagen fibers, possibly due to the formation of ammonia.

It is not our purpose to discuss the merits of commercial bates, but the question naturally arises as to what is the effect of the large amount of ammonium chloride which they contain. A sample which we believe contained pancreatin was found to have no elastin-digesting power at any concentration. It was our first thought that the trouble was due to too high a ratio of ammonium chloride to enzyme, but the preparation was still quite without action after the salt had been removed by dialysis. The real cause may have been the presence of much woody fiber used as a filler. If protein can remove the enzyme from the field of action, it is possible that woody fibers can also and, if these have an isoelectric point much removed from that of the protein, it is possible that at any concentration or at any pH value, a greater proportion of enzyme to woody fiber would be required than the sample contained.

Effect of Elastin Removal

A limed calfskin was cut into halves along the line of the backbone, the elastin was completely removed from one half by means of pancreatin, while the other half was simply treated with dilute ammonium chloride solution having a pH value of 8 in order to reduce its swelling to a minimum. Both halves were then thoroughly washed. It was recognized that an exact comparison of the two halves during tanning could not be made, if the pH values of the absorbed water were very different. Every effort was made to have the pieces identical, excepting for elastin content.

The most noticeable difference was observed during the early stage of vegetable tanning. The surface layers of the skin naturally tan more rapidly than the fibers in the interior and there is a tendency for the grain surface to expand temporarily to a greater extent than the rest of the skin. The elastin fibers in the unbated half evidently tended to prevent this expansion and the result of the tension produced was a slightly harsh feel, although the grain appeared tight and smooth to the eye. The grain of the completely bated half, however, actually expanded, giving the skin temporarily a wrinkled appearance, although the grain felt very soft and silky. When both halves had become completely tanned, this difference had almost disappeared. In the finished leather, the only difference in appearance was a slightly lighter color in the bated half. Photomicrographs

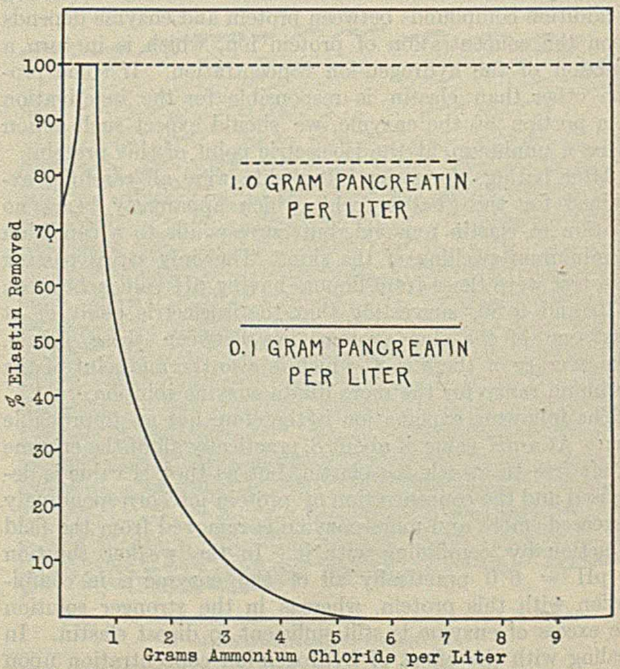

Fig. 7—Removal of Elastin Fibers from Limed Calfskin as a Function of the Concentration of Ammonium Chloride. Time of Digestion 24 Hrs.; Temperature 40°; pH Value 7.6

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[1] *J. Am. Chem. Soc.*, **39** (1917), 1501.

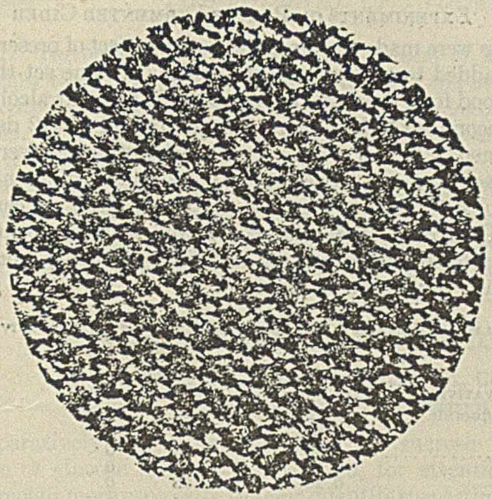

FIG. 8—GRAIN SURFACE OF FINISHED CALF LEATHER WITH NONE OF ITS ELASTIN REMOVED. MAGNIFICATION, 15 DIAMETERS

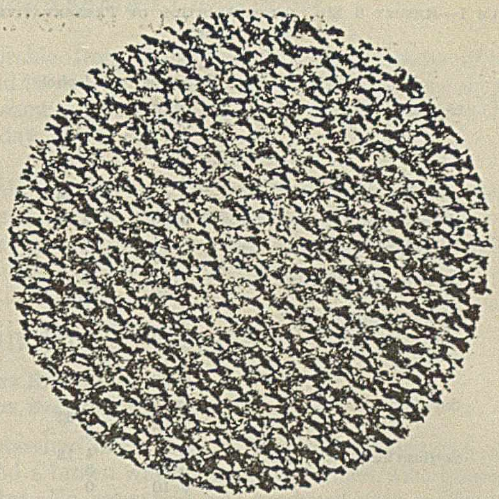

FIG. 9—GRAIN SURFACE OF FINISHED CALF LEATHER FROM WHICH ELASTIN HAS BEEN ENTIRELY REMOVED. MAGNIFICATION, 15 DIAMETERS

of exactly corresponding points on the grain surface of the two halves are shown in Figs. 8 and 9.

While bated and unbated finished leathers appear much alike to the eye, there are perceptible physical differences such as one might expect to find in view of the fact that the elastin fibers have been removed from under the grain of the bated leather. The desirability of completely, or even partially, removing elastin from skin depends upon the use to which the leather is to be put.

SUMMARY

A critical study of bating has been made which tends to elevate a heretofore mysterious process to a scientific plane.

The primary function of bating is to remove elastin fibers from the skin prior to tanning.

When a dilute solution of pancreatin was employed, complete digestion of the elastin was effected only when the pH value of the solution lay between 7.5 and 8.5, but when a more concentrated solution was used, the range was extended to 5.5 and 8.5. An explanation of this is given on the assumption that an addition compound between the enzyme and protein other than elastin is formed in increasing amounts as the pH value is reduced from 8.

The rate of removal of elastin from calfskin is shown as a function of the concentration of enzyme and of the time of digestion.

Ammonium chloride shows an activating effect in concentrations up to 0.5 g. per liter and a marked inhibitory effect in higher concentrations.

The failure of commercial bates to remove elastin from calfskin is attributed to the presence of woody fibers.

A comparison of bated and unbated leathers is made.

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NOTE: Since submitting this paper for publication, we have received an interesting communication from L. Krall of Geneva, Switzerland, bearing upon the subject. Having just seen the German translation of our first paper, he has written to claim priority in discovering, by means of the microscope, that the chief function of bating is the removal of elastin fibers from the skin. His experiments, performed at the University of Geneva from 1914 to 1916, proved that the elastin fibers of skin can be entirely removed by digestion in an infusion of dog dung at 40°. His photomicrographs show that the action of dung is practically identical with the action we found for pancreatin, thus furnishing further evidence of the soundness of Wood's conclusion that pancreatin is the active constituent of dung in bating. We did no experimenting with dung. Krall's important paper was unfortunately buried in a private bulletin published by the *Société Anonyme, anc. B. Siegfried,* of Zofingue, Switzerland, in June 1918, and we were not aware of its existence until his communication was received.

Cider Preservatives[1]

By R. D. Scott and E. G. Will

STATE DEPARTMENT OF HEALTH, COLUMBUS, OHIO

The alcoholic content of cider having become of some importance with the advent of the Eighteenth Amendment, the need exists for an efficient preservative, both to prevent fermentation of fresh cider and for court work, to hold the alcoholic percentage of seized samples unchanged pending analysis.

Sodium sulfite, sodium benzoate, and salicylic acid are known to be used commercially for preserving cider, but no literature concerning any except sodium benzoate could be found. Accordingly, the following experimental work was undertaken.

EXPERIMENTS ON FRESH CIDER

The cider used was prepared by the writers from reasonably sound, unwashed, and unpared apples, of which ten varieties were used. From this stock, 400-cc. portions were transferred to 500-cc. flasks which were loosely stoppered after the addition of the preservatives, and were placed in a dark cupboard. Both alcoholic and acetic fermentation would probably be more rapid under such conditions than if barrel lots had been used, thus subjecting the preservatives to more rigorous tests than might be the case in practice. Alcohol (per cent by volume) and acidity (g. per 100 cc. as acetic) were determined at intervals of 2 wks., 2 mo., and 6 mo. The room temperature during this period ranged from 18° to 25° C. Results after 6 mo. only are recorded in Table I, in which Samples 1 to 11 and Control A represent one lot of juice; Samples 12 to 18 and Control B, a different lot of juice, expressed 1 wk. later from the same lot of apples.

RESULTS—Saccharin, formaldehyde, sodium hypochlorite, and β-naphthol were not effective in preventing alcoholic fermentation when used in amounts up to 0.1 per cent.

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[1] Received August 1, 1921.

TABLE I—RESULT 6 MO. AFTER ADDITION OF PRESERVATIVES TO FRESH CIDER

SAMPLE	PRESERVATIVE	Amount Added Per cent	Alcohol	Acidity
1	Sodium sulfite	0.10	0	5.18
		0.20	6.40	0.30
2	Boric acid...............	0.10	1.70	3.26
		0.20	3.44	0.32
3	Borax....................	0.10	0	4.76
		0.20	4.69	0.82
4	β-Naphthol...............	0.10	0.84	5.14
5	Chlorazene...............	0.01	0	5.94
		0.10	0	0.98
6	Sodium hypochlorite[1]......	0.01	0	1.06
		0.10	4.90	0.35
7	Sodium benzoate..........	0.02	0	0.96
		0.04	0	1.08
		0.07	0	1.12
		0.10	0	2.66
		0.20	0	1.06
8	Salicylic acid[2]............	0.07	0	3.71
		0.10	5.62	0.38
		0.20	0	0.43
9	Sodium fluoride..............	0.04	4.18	0.42
		0.07	0	0.28
		0.10	0	0.30
10	Thymol...................	0.04	0	1.06
		0.07	0	0.40
		0.10	0	0.40
11	Mercuric chloride.........	0.025	0	0.44
		0.05	0	0.50
		0.10	0	0.48
Control A	None	....	6.50[6]	0.40[7]
				5.30[8]
12	Resorcinol...............	0.10	6.48	0.78
		0.20	6.70	0.84
13	Salol....................	0.10	5.92	0.98
		0.20	5.91	0.98
14	Saccharin................	0.05	6.15	0.94
		0.10	6.28	0.85
15	Formaldehyde[3]...........	0.05	0.15	1.44
		0.10	3.85	0.66
16	Sodium hydroxide.........	0.50	0	1.18
17	Hydrogen peroxide[4].......	0.10	0	3.41
		0.20	0	0.24
18	Copper sulfate[5]...........	0.005	3.38	0.90
		0.01	0	1.20
Control B	None	....	7.50[6]	0.41[7]
				3.60[8]

[1] As available chlorine.
[2] Acidity is corrected for amount of salicylic acid present.
[3] As 40 per cent solution.
[4] As 3 per cent solution.
[5] As copper.
[6] Maximum.
[7] Initial.
[8] Final.

Sodium sulfite, borax, boric acid, resorcinol, and salol were not effective in amounts of 0.2 per cent. Sodium hydroxide (0.5 per cent), hydrogen peroxide solution (0.1 per cent), chlorazene (0.1 per cent), and copper sulfate (0.01 per cent as metal) checked alcoholic, but did not prevent considerable acetic, fermentation. As, in our opinion, all the above substances would have to be effective in smaller amounts than recorded to be of much value as preservatives, no further study of them was made. Mercuric chloride (0.025 per cent), thymol (0.07 per cent), and sodium fluoride (0.07 per cent) were effective in preventing both alcoholic and acetic fermentation.

Sodium benzoate in amounts as low as 0.02 per cent prevented any appreciable amount of alcohol from forming, not more than 0.1 per cent being present at any period, but even when used to the extent of 0.2 per cent did not prevent acetic fermentation. Gore[1] records similar results for sodium benzoate.

Salicylic acid (0.2 per cent) was effective in preventing alcoholic and acetic fermentations, but was not effective in 0.1 per cent strength. It may be noted that certain preservatives, in sufficient concentration, did not prevent complete alcoholic fermentation, but retarded or prevented acetic fermentation. It is also a point of interest that samples treated with boric acid and with borax developed a strong odor of ethyl acetate. The volatile ester content of the sample containing 0.2 per cent boric acid was found to be 0.86 g. per 100 cc., calculated as ethyl acetate.

EXPERIMENTS ON PARTLY FERMENTED CIDER

Tests were made to determine also the effect of preservatives when added to partly fermented cider. In one set the cider had stood for 3 days and contained 0.22 per cent alcohol, and in a second set it had been allowed to stand for 12 days and contained 3.00 per cent. Two stocks of juices were used, expressed from the same lot of apples, but at different dates. Control A represents the juice containing 0.22 per cent alcohol; Control B, the juice containing 3.00 per cent. The result after 6 mo., which did not differ markedly from those at 2 mo., are shown in Table II.

TABLE II—RESULTS 6 MO. AFTER ADDITION OF PRESERVATIVES TO PARTLY FERMENTED CIDER

PRESERVATIVE	Amount Added Per cent	Alcohol Initial	Alcohol Final	Acidity Final
Sodium fluoride.....	0.10	0.22	1.05	0.42
	0.20	0.22	0	0.48
Thymol............	0.05	0.22	0	0.44
	0.10	0.22	0	0.44
	0.20	0.22	0	0.40
Sodium benzoate....	0.10	0.22	0	1.12
	0.20	0.22	0	1.14
Salicylic acid[1].......	0.05	0.22	2.82	1.33
	0.10	0.22	0	0.46
	0.20	0.22	0	0.41
Control A, none			5.93[2]	0.40[3]
				3.00[4]
Sodium fluoride.....	0.10	3.00	0.42	2.92
	0.20	3.00	0	3.10
Thymol............	0.10	3.00	2.51	0.43
	0.20	3.00	2.82	0.44
Sodium benzoate....	0.10	3.00	0	2.84
	0.20	3.00	0	3.08
Salicylic acid[1].......	0.10	3.00	0	3.20
	0.20	2.00	2.32	0.42
Control B, none			7.72[2]	0.52
				4.80

[1] Acidity is corrected for amount of salicylic acid present.
[2] Maximum.
[3] Initial.
[4] Final.

In the case of the cider containing 0.22 per cent alcohol, 0.05 per cent of sodium benzoate prevented the formation of additional alcohol, but 0.2 per cent did not prevent acetic fermentation.

Sodium fluoride (0.2 per cent), salicylic acid (0.1 per cent), and thymol (0.05 per cent) were effective in preventing further fermentation.

In the case of the cider containing 3.00 per cent alcohol, neither sodium benzoate nor sodium fluoride (0.2 per cent) prevented the formation of acetic acid. Thymol (0.1 per cent) and salicylic acid (0.2 per cent) were effective in holding the alcohol nearly unchanged and in preventing acetic fermentation. It required more of a given preservative to prevent change in partly fermented than in fresh cider.

For the purpose of preserving samples for analysis, thymol, salicylic acid, and probably mercuric chloride are effective. The latter has the disadvantage of being poisonous; since the chemist who examines a liquor is usually called on to state whether it is palatable and fit for beverage purposes, its use is not to be recommended.

Thymol, while effective, has the slight objection that it comes over in the distillate even when the sample has been neutralized, thus necessitating a second distillation with an excess of alkali.

Salicylic acid is, in our opinion, the most satisfactory preservative for samples to be used in court work, 0.2 per cent being sufficient. It is not dangerous to taste samples containing this amount, none distils over from the neutralized sample, it may be obtained from any druggist, and the amount present in the sample may readily be ascertained.

As regards finding a satisfactory preservative for commercial purposes, our results are not particularly encouraging. The use of sodium benzoate has some official sanction, but while small amounts prevent any appreciable alcoholic fermentation, acetic fermentation proceeds practically un-

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[1] U. S. Bureau of Chemistry, *Bulletin* 118.

checked. Nevertheless, it is a practical means of keeping cider below the 0.5 per cent alcoholic limit, and the beverage thus treated could be safely dispensed until too sour to be palatable. The addition of 0.05 per cent of the preservative to the fresh juice should be sufficient.

While salicylic acid is not considered more harmful than other preservatives,[1] it has not been received with much favor. It would probably have to be used to the extent of 0.1 per cent, an amount probably somewhat too high to be desirable from a physiological standpoint. However, it should be mentioned that tests described in the above reference show only a slight ill effect from the ingestion of 1 g. per day for 30 days.

CONCLUSIONS

1—Salicylic acid 0.2 per cent or thymol 0.1 per cent will preserve cider effectively for the purpose of court work.

2—For preserving cider commercially, sodium benzoate and salicylic acid are of some value.

A New Qualitative Test for Sucrose in the Presence of Glucose[2]

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Comparatively few qualitative tests for sucrose in the presence of glucose have been developed, for attention has been directed more especially to their quantitative estimation. The determination of specific rotation or reducing power before and after inversion with hydrogen chloride or invertase has been of value in the past as a means of identification. In considering the specific rotation of mixtures of sucrose and glucose in a compound of unknown composition, we must not lose sight of the fact that foreign optically active substances would influence this value. In selecting the reduction method, it must be taken into account that there is a slight reduction of copper by sucrose in the presence of invert sugar.[3]

In the color reactions with phenols in presence of concentrated acid, used for the identification of sugars, the development of the color is said to be due to the formation of condensation products between the phenol derivatives and the decomposition products obtained from the sugar (humus substances, furfural, aldehydes, etc.). The most important phenol derivatives used for color reactions with sugars are α-naphthol, thymol, resorcinol, orcinol, naphthoresorcinol, and phloroglucinol.

The α-naphthol method described by Rapp and Reseinfelder[4] and others[5] is extremely delicate for sucrose solutions, but, according to C. A. Browne,[6] the deep violet coloration is also given by solutions of invert sugar. The tints given by other phenol derivatives vary from cherry-red to deep purple. The coloration which sucrose gives with morphine, codeine, aconitine, veratrine, and other alkaloids, in presence of sulfuric acid is also given by invert sugar, the same being true for the coloration given with ammonium molybdate[7] in presence of sulfuric acid.

C. Reichard[8] has suggested the use of sodium arsenate or tannic acid in the presence of hydrogen chloride for the detection of sucrose, but the value of this test is undetermined as yet. The work of Reichard upon the reactions of carbohydrates showed that, in the cold, sulfuric, nitric, or hydrochloric acid converted sugar into a pasty mass, which did not dry in the air. Carbonaceous matter produced by the sulfuric acid did not separate until the mixture was heated. The green coloration of copper sulfate in hydrochloric acid was retained much longer when sucrose was present, and it inhibited somewhat the precipitation produced by the acid when added to mercurous nitrate. In the presence of hydrochloric acid, sucrose yielded a dark green coloration with potassium bichromate, a blue with ammonium molybdate, and a brown which changed to violet with ammonium vanadate. No coloration was produced with sodium tungstate or titanic acid in the presence of sulfuric acid. Sodium arsenate and hydrochloric acid gave a rose-red coloration with sucrose. Of the colorations produced with organic bodies, the most marked was the red with tannic acid in the presence of hydrochloric acid. The author points out the value of this tannic acid test, the resorcinol color test, and the arsenic acid reaction for the detection of sucrose.

Wiley[1] has suggested a qualitative test for sucrose in the presence of glucose. The sugar is treated with cobaltous nitrate and potassium hydroxide, after dextrin or gums have been removed with alcohol. Sucrose will produce a permanent amethyst-blue color while glucose will give a turquoise blue, passing over to a light green. In a mixture of these two sugars, the color due to sucrose will predominate, if not less than 10 per cent of the sucrose is present.

To discover a new method for the qualitative detection of sucrose, a study of the action of various organic solvents upon glucose and sucrose was made.

EXPERIMENTAL

The substances tested were sucrose and glucose whose impurities were less than 1 per cent. The reagents used for extraction were *n*-amyl alcohol, benzene, toluene, *p*-xylene, carbon bisulfide, ligroin, carbon tetrachloride, acetic acid, acetone, and ethyl acetate. No work was done with methanol, ethyl alcohol, ether, and chloroform, since their action has been thoroughly investigated and it has been found that sucrose and glucose are *both* insoluble in ether and chloroform, soluble in varying degrees in ethyl alcohol, and insoluble in methanol. The solvents had been redistilled and only those portions which boiled at the temperatures given in the accompanying table were employed in the experiments. A known weight (1 g.) of the sugar was taken, and the volume of the solvents used was 100 cc.

SOLVENT	BOILING POINT	GLUCOSE	SUCROSE
n-Amyl alcohol	137	Soluble	Soluble
Acetic acid	118	Soluble	Soluble
p-Xylene	138	Insoluble	Insoluble
Toluene	111	Insoluble	Insoluble
Ligroin	90	Insoluble	Insoluble
Benzene	80	Insoluble	Insoluble
Carbon tetrachloride	76	Insoluble	Insoluble
Carbon bisulfide	46	Insoluble	Insoluble
Acetone[1]	56	Soluble (variable)	Insoluble (variable)
Ethyl acetate	74	Soluble	Insoluble

[1] There is an appreciable variation in the amounts of glucose and sucrose extracted by acetone, the former being more soluble.

The dry sucrose and glucose were placed separately in filter paper extraction thimbles. An ordinary Soxhlet extraction tube with reflux condenser, cooled by running water, was used for extraction. A small Bunsen burner was used to bring the organic solvent to the boiling point, and to keep the solvent boiling until the experiment was completed.

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[1] U. S. Bureau of Chemistry, *Bulletin* **8A**, II, 757.

[2] Received June 9, 1921.

[3] G. L. Spencer, "Handbook for Cane Sugar Manufacturers and Their Chemists," J. Wiley & Sons, **1912**, 91.

[4] *Deut. Zuckerind.*, **1892**, 538.

[5] *Monatsh.*, **6** (1885), 198; abstr. *J. Chem. Soc.*, **50** (1886), 923.

[6] "Handbook of Sugar Analysis," J. Wiley & Sons. **1912**, 681.

[7] *Bull. assoc. chim. sucr. dist.*, **27** (1909), No 3, 179; abstr. *Chem.-Ztg.*, **33** (1909), 538.

[8] *Pharm. Zentralhalle*, **51** (1910), 979; abstr. *J. Chem. Soc.*, **98** (1910), 1117; abstr. *Expt. Sta. Record*, **25**, No. 9, 801.

[1] "Principles and Practice of Agricultural Analysis," III, p. 189, The Chemical Publishing Co., **1908**.

The time of extraction was 5 hrs.

The results of these extractions are shown in the table, in which the terms soluble and insoluble are used to show whether or not extraction was possible.

As noted in the table, glucose is almost completely extracted by ethyl acetate while sucrose is but slightly affected. A run was made using equal parts of the glucose and sucrose, duplicating the results already given. Upon cooling the ethyl acetate solution of glucose, crystals of this substance were formed.

Further work is being done to determine the value of ethyl acetate in the quantitative estimation of mixtures of glucose and sucrose, and also on the use of this organic solvent for the actual preparation of crystalline glucose. It is also contemplated to include in this work, mixtures of other sugars, such as fructose and other less common sugars. The effect of traces of water on the solubility of the various sugars in ethyl acetate will also be investigated.

SUMMARY

1—Ethyl acetate may be used as a reagent for testing a dry mixture of glucose and sucrose by the extraction method, affording a new qualitative test for the separation of glucose and sucrose in mixtures.

2—Further work is being done to determine the value of ethyl acetate in the separation of glucose from other sugars, the separation of sucrose from fructose, etc., the use of ethyl acetate for the quantitative estimation of the sugars, the use of this solvent in the preparation of crystalline glucose, and the effect of traces of water on the solubility of the various sugars in ethyl acetate.

Potash Shales of Illinois[1]

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Investigation of the potash shales of Illinois was taken up in 1917 in an effort to find values in the residues from certain shales which were under investigation in the laboratory of applied chemistry at the University of Illinois, with primary reference to the amount of oil to be obtained on destructive distillation. The shale from one region, Johnson County, yielded from 45 to 50 gal. of oil per ton and would therefore be of interest for its oil yield alone. Other shales which were of questionable value from the standpoint of oil yield might come into the field of possible technical utilization if other values could be discovered in them. This constituted a primary reason for examining all samples for other values, such as phosphorus and potash. The samples, eighteen in all, were furnished through the courtesy of the Illinois State Geological Survey. They came from localities widely distributed over the state. None of the samples contained phosphorus in more than a trace. Although the majority contained 2 or 3 per cent of potash (K_2O), which is normal for shale rock, two formations showed a potash content of from 5 to 5.8 per cent (K_2O). Of these latter two, the more important is a black carbonaceous shale which outcrops at frequent intervals over a distance of about 7 mi. in Union County. The other is a green sandy shale of entirely different character occurring in Lee County near Dixon, Ill.

POTASH SHALES IN CEMENT MANUFACTURE

From a study of the potash situation it would seem that one of the hopeful sources for a domestic supply resides in the recovery of potash as a by-product from the manufacture of cement. Even though the average shale used in the cement mix does not contain more than 1.5 to 2.5 per cent of potash (K_2O), the potential supply from this source would be very great, as a result of the tremendous tonnage of cement being produced.

The Illinois shales that we are here considering, instead of having an average potash content of 2 or even 2.5 per cent, have a content of 5 per cent. They compare, therefore, very favorably with the greensands of New Jersey.[2] The first question that naturally arises, therefore, relates to the suitability of these Illinois shales for the purpose of compounding a suitable cement mix.

Illinois shales of suitable composition for cement making, according to Bleininger,[3] are shown in Table I. For comparison, two of the high potash shales are shown in parallel columns.

TABLE I—COMPARISON OF ILLINOIS SHALES WITH REFERENCE TO THEIR CEMENT-MAKING PROPERTIES

CONSTITUENT	Average of 8 Illinois Shales (Bleininger)	Illinois Potash Shales Sample 1	 Sample 2
SiO_2	61.56	53.8	55.0
Al_2O_3	16.12	17.7	16.3
Fe_2O_3	2.96	5.8[1]	6.0[1]
FeO	3.52	...	...
CaO	0.94	0.7	0.3
MgO	1.79	1.8	1.5
K_2O	2.90	5.0	4.9
Na_2O	0.82	0.5	0.4
Ignition loss	6.72	11.9	13.0

[1] Total iron calculated to Fe_2O_3.

Samples 1 and 2 are the black carbonaceous shale from Union County. It will be observed that, except in potash content, they vary but little in composition from the average of other shales which are said to be suitable for cement making. Their high potash content might be an advantage also in the formation of the clinker, since it would tend to lower the burning temperature.

Other factors which are important in evaluating these shales for cement-making purposes are as follows:

	Sample 1	Sample 2
Silica-alumina ratio	3.02	3.37
Inert mineral content	0.63	0.75
Sulfur	2.40	2.80

The silica-alumina ratio is in the most advantageous zone, and the inert mineral content is low. The sulfur occurs principally in microscopic form as pyrite.

In average American practice the raw mix will contain 0.7 to 1.0 per cent of K_2O. On the basis of 65 per cent recovery, which according to Huber and Reath[1] it seems reasonable to expect, there would result an average yield of 2.9 lbs. of potash per barrel of cement. On the same basis, the potash shales whose analyses are given in Table I should yield 5.4 lbs. per bbl.

One other region in the state has thus far supplied a shale with a high potash content, but its cement-making possibilities have not been determined. This shale, from Dixon, in Lee County, contains 5.8 per cent of potash. It is coarse-grained and friable. While its green color is suggestive of the greensands of the East, the geological character of the material is quite different, as will be shown later.

CONSTITUTION OF ILLINOIS POTASH SHALES

The shales from Union County are peculiar in that they contain a small percentage of oil, present in the free state. This has no industrial significance, but it adds to the other volatile constituents, such as water of hydration, so that the reduction in weight upon ignition, as shown in Table I,

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

[2] *Chem. Met. Eng.*, **22** (1920), 815.

[3] Illinois State Geological Survey, *Bulletin* **17** (1912).

[1] *Chem. Met. Eng.*, **16** (1917), 702.

amounts to about 12.5 per cent of the raw material, and the potash content of the residue becomes 5.75 per cent. With the Dixon shale but little loss occurs on ignition, and the potash percentage is about the same in either the ignited or the raw state.

ACTION OF SULFURIC ACID—No very simple or direct method was available for determining the form of combination in which the potash was held. One procedure consisted in digesting 1 g. of the sample with 25 cc. of concentrated sulfuric acid, heating until about half of the acid had been removed, diluting, filtering, washing, and igniting the residue, and analyzing it for total potash. The percentage of potash found was considered as being in some other than the feldspathic form.

By this procedure 62 per cent of the total potash was found to be removed from the Union County shales, while from the Dixon shale only about 15 per cent was removed, showing a marked difference in the chemical composition of the two shales. Further proof of this difference was desired. It is true that in the process of cement manufacture the potash would be equally recoverable in either case; but from any other standpoint differences in the ease with which the potash might be removed by chemical solvents, or concentrated into a form for more ready extraction, might make a wide difference in the value of the shales from the two sources.

It is not the purpose of this discussion to go into the details of the experiments to determine the chemical character of the potash-bearing constituents. The method of analysis suggests that the potash in the Dixon shale is chiefly or altogether feldspathic in combination, and that the major part, at least, of the potash in the Union County shale is in some combination more nearly resembling the glauconitic or greensand formations. These formations are considered as being potassium-iron silicates with an average potash content varying from 5 to 7 per cent K_2O.

MICROSCOPIC EXAMINATION—Thin sections for study under the microscope were prepared. No very positive information came from such studies. In general it seemed evident that the Union County shales had passed through extensive secondary decompositions and that the Dixon shales had not. Both types, however, even in the undisturbed condition of the deposits, had their ultimate particles in such a finely divided state as to render impossible their re-solution and study under the microscope.

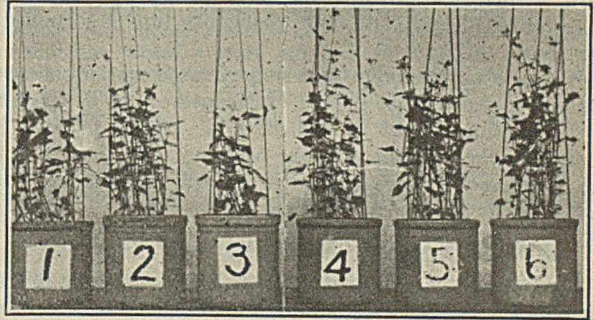
TESTS WITH PLANTS—A third method of study into the probable type of composition was as follows: Accepting the generally conceded fact that potash in feldspathic combination is only slightly, if at all, available directly as plant food, further data on composition might be obtained from experiments to determine whether some of the potash in the Union County shales was directly available for plant use. Some foundation for this theory was already afforded by the fact that 62 per cent of the total potash was soluble in acid. If the Union County shales were treated with strong acid in such a manner as to remove all their acid-soluble potash, and if the residue with the remaining 38 per cent of potash (presumably in feldspathic combination) were submitted to plant action and found lacking in available potash, this would afford a still further proof in the chain of evidence as to the type of potash combination in the original shale.

It is not our purpose to go into the details of the results from these pot cultures, which were conducted by the Agronomy Department of the College of Agriculture, further than to correlate the results, so far as they have a bearing upon the composition of the shales.

In Table II there is shown the behavior of the various shale materials when applied to a peat soil deficient in potash. Buckwheat was selected as the plant most responsive to the varying treatments. An equivalent quantity of potash was added in each case, except to the check pots which, of course, contained no added potash in any form. Each pot was made up of 7 kg. of peat soil, 60 g. of pulverized limestone, and the various types of shale material, ground to pass a 100-mesh sieve, and in an amount that would carry into the soil mixture in each case a total potash content of 1.61 g. (K_2O).

TABLE II—COMPARATIVE STUDY OF BUCKWHEAT GROWTH, USING SHALE MATERIALS OF DIFFERENT COMPOSITION

No.	DESCRIPTION OF POTS	CONDITION OF PLANTS SIX WEEKS AFTER PLANTING
1	Check pot using peat soil with insufficient potash	Poor growth
2	Peat soil as in 1, with Dixon shale	Poor growth, not distinguishable from No. 1
3	Peat soil as in 1, with Union County shale, less 62 per cent of potash by acid extraction	Poor growth, not different from Nos. 1 and 2
4	Peat soil as in 1, with Union County shale ignited	Excellent growth more dense and taller than Nos. 1, 2, or 3
5	Peat soil as in No. 1, with Union County shale, Sample 1 not ignited	Excellent growth, not distinguishable in density or vigor from No. 4
6	Peat soil as in 1, with Union County shale, Sample 2 not ignited	Excellent growth, equal in every respect to Nos. 4 and 5



BUCKWHEAT PLANTS GROWING ON PEAT SOIL TO WHICH VARIOUS SHALE MATERIALS HAVE BEEN ADDED

1—Check
2—Dixon shale
3—Union Co., acid-extracted
4—Union Co., ignited
5—Union Co., No. 1, not ignited
6—Union Co., No. 2, not ignited

This amount of potash represents the weight per acre that would be present in a normal soil which was deemed to have an adequate supply of that constituent. The results presented in the table are also clearly shown in the photographic reproduction.

Pot 1 is the check, with deficient potash. Pot 2 has the standard equivalent of 1.61 g. of K_2O added in the form present in the Dixon shale, and Pot 3 has the same addition in the form of acid-insoluble residue from the Union County shale. An examination of these three pots seems to warrant the conclusion that potash in any available form is lacking in each case. This, therefore, would seem to confirm the previous assumption that the potash present in Pots 2 and 3 is in the feldspathic form.

By further reference to Pots 4, 5, and 6, there is an equally obvious indication that in these pots potash is present in a form available for plant use; and since the only variable in the experiment is the acid-soluble constituent, it is evident that the potash utilized by the plant comes from this source.

Moreover, ignition or non-ignition of the shale does not affect the property of the potash so far as food availability is concerned. It would be of scientific interest, of course, to be able to say more definitely in what form was the potash combination here found. We have compared it thus far in the discussion to the greensands of the eastern United States which are true glauconites. The most that can be said of these shales is that they are glauconitic in type. They may have been originally a feldspathic deposition which has undergone secondary decomposition *in situ*. Indeed, the region has other striking examples of decomposition, for example, the very pure deposits of amorphous silica, found so abundantly in Union County, as well as some very pure kaolins.

So far as conformity to greensand or glauconitic conditions is concerned, there is every justification for such a classification, as may be seen from the following quotation,[1] indicating the geological conditions under which the true glauconites are supposed to have been formed:

> The organic matter transforms the iron into sulfide which may be oxidized to hydrate, sulfur being at the same time liberated. This sulfur would oxidize to sulfuric acid, which would decompose clay, setting free colloidal silica, aluminium being removed in solution. Thus, we have colloidal silica and hydrated iron in a state most suitable for their combination. The potash which is necessary to complete the composition of glauconite may be derived from the decomposed fragments of crystalline rocks like orthoclase or white mica.

Upon analysis of the shale for iron in the pyritic form by methods developed in this laboratory,[2] it appears that when the pyritic iron is deducted from the total iron of the shale there remains 3.8 per cent of iron available for combination with the 3.1 per cent of potash present in the acid-soluble form, an amount which approaches the ratio for glauconitic material with sufficient approximation to warrant the classification thus proposed, *viz.*, not true glauconite but glauconitic in type.

We have noted above that some free oil was found to be present in these black shales. It is interesting to speculate as to whether or not in this material, potash feldspar has changed over into shale in the ordinary way, but that the free oil present has prevented the removal of the more soluble materials by an excess of water.

Extraction and Concentration of the Potash

The peculiar character of these shales, which seem different from any potash material which the authors have found described in the literature, would seem to warrant a search for some direct method for the extraction of the potash. The facts already presented coupled with the results of other work that we have done preclude the possibility of finding a successful method. Only two-thirds of the total potash content of the rock can be extracted with acids under any conditions. The fine grain and uniform distribution of the potash-carrying constituent make it impossible to bring about any mechanical separation.

Conclusions

1—In at least two localities in Illinois, shales occur which contain 5 per cent or more of potash.

2—Shale outcropping in several places near Jonesboro, in Union County, which contains 5 per cent of potash would be suitable, so far as can be determined from its chemical composition and physical character, for use in the manufacture of portland cement.

3—By using this material in the manufacture of cement and by applying the known methods of potash recovery, a yield of 5.3 lbs. of potash per barrel of cement could be obtained.

4—The constitution of the southern Illinois shale is complex. The shale contains free oil, bituminous matter, pyrite, undecomposed potassium-bearing rock, feldspathic in character, and potassium-bearing material of the nature of glauconite or greensand.

5—Shale from Dixon, Lee County, contains 5.8 per cent of potash, which is held for the most part in a more stable condition than that in the southern Illinois shale.

6—Extraction of the potassium from shale of either the southern Illinois or the Dixon type by means of solid or liquid reagents would seem to be impracticable, because of the cost of leaching and recovering potash from material where it is present in such small amounts.

7—The plant availability of the potash in the southern Illinois shale is probably characteristic of all the material of this type outcropping in that locality.

8—That part of the potassium in the southern Illinois shale which is soluble in sulfuric acid is shown to be in a combination of the glauconite type.

9—In southern Illinois shale having a potash content of 5.0 per cent in the raw condition or 5.6 per cent when ignited, 62 per cent of the total potash is glauconitic in character and is available as plant food.

The Determination of "Strength" or Neutralizing Power of Acid Calcium Phosphates[3]

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Acid calcium phosphate has been used for a number of years in leavening powders and self-raising flours. Its function is of course purely that of an acid to liberate carbonic acid gas from sodium bicarbonate, and its capacity to do this is a prime factor in determining its value.

Its neutralizing strength is usually stated in terms of sodium bicarbonate, that is, the number of parts of bicarbonate neutralized by 100 parts of the acid phosphate.

Simple as such a determination may at first sight appear, there is more or less controversy over this matter.

History of Controversy

Comparatively few chemists have had experience with the chemistry of acid phosphates. Such as have had this experience have generally been connected with one or another manufacturer in a highly competitive business, and it has come about that the question of how the "strength" of acid phosphates should be determined is no longer a purely scientific one but is a factor in competitive trade.

Extraordinarily little has been published on the subject of the analysis of acid phosphates. Apart from a paper by Chas. A. Catlin and one by the present writer, both published about twenty years ago,[1] hardly anything on the subject has appeared in chemical literature.

Acid calcium phosphate was originally prepared as a substitute for cream of tartar in leavening powders, and for this purpose its strength was adjusted (by the addition of starch) to equal that of cream of tartar, *viz.*, 100 parts to neutralize 44.6 parts of bicarbonate, or the strength or "titration" was made "45" and for many years this was the regular and established custom of the trade. There was little or no dispute as to the strength, and the regular method of determining such strength was the obvious one of direct titration with standard alkali.

Competitive conditions, however, led the manufacturers to seek selling levers by which to boost their particular makes. Color, physical condition, absence of "free acid," and other points were in turn duly exploited until some maker hit upon "strength." By leaving out some of the starch it was easy to offer goods of 50 strength. Goods of 55, 60, and higher strengths were successively offered to the trade, until eventually all starch was omitted and the present form of starchless

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[1] W. B. Clarke, *J. Geol.*, **13** (1900), 509.

[2] A. R. Powell, with S. W. Parr, University of Illinois Engineering Experiment Station, *Bulletin* **111** (1919).

[3] Received July 5, 1921.

[1] Catlin, *J. Anal. Chem.*, **4**, Part 4 (1890); Wadman, *J. Am. Chem. Soc.*, **16** (1894), 333.

acid phosphate became common. With the complete elimination of starch, no further increase of strength could be obtained. But the necessity remained of having some selling point over competitors, and there arose a number of fantastic methods of determining the "strength" of acid phosphates.

All such methods have two points in common: Without exception they studiously introduce conditions totally unlike those occurring in practice, when the material is used in the actual baking operation, and, also without exception, they give higher results than tests made as nearly as may be under baking conditions. All such departures from a simple titration, conducted as nearly as may be under the conditions of actual baking practice, are made solely for the purpose of allowing the analyst to record higher "strengths." At any rate, the writer has yet to learn of any method being advocated that yielded lower results than simple, direct titration.

CHEMICAL CONSIDERATIONS

At first glance it would seem impossible that there could be any great uncertainty in determining the acid strength of an acid substance. With cream of tartar, for instance, only one reaction is possible and the result is practically the same, no matter how varied the conditions of analysis as to dilution, temperature, direct or indirect titration, amount of indicator present, etc.

Phosphoric acid, however, admits of considerable variation in result, depending on the conditions of manipulation. The end-product may be either a di- or triphosphate (R_2HPO_4 or R_3PO_4), or it may be something between these two.

Normally, phosphoric acid tends to give a dibasic salt when neutralized by alkalies, and salts of this type are by far the most common. While the salts of the R_2HPO_4 form are still, strictly speaking, "acid" salts, in that there is still one atom of basic hydrogen present, they are not acidic in character but rather slightly alkaline, and will not displace carbonic acid from carbonates except under conditions far removed from those of the baking process. There are of course a number of tribasic phosphates, but in most cases special pains must be taken to bring about their formation. The third molecule of base is generally very feebly combined and often behaves (as in the trialkali phosphates) practically like a free base.

Acid calcium phosphates when neutralized tend to form mostly dicalcium phosphate, or possibly an intermediate between di- and tricalcium salt, but nearer the dibasic salt.

The basicity of the end-products can, however, be increased by various expedients, all more or less drastic, and differing from the conditions obtaining in actual use, and the measure of the increase in basicity of end-products is roughly proportional to the degree of difference.

Favorite methods to obtain this end are titration under excessive dilution, indirect titration using a large excess of alkali and boiling in the presence of this excess of caustic alkali, excessive heating, addition of foreign salts, etc. Very helpful to some of these methods is the fact that calcium phosphate goes down as a semigelatinous precipitate which adsorbs the indicator and inhibits the appearance of the color reaction unless considerable indicator is present. By using a very small amount of indicator (phenolphthalein) it is possible to obtain a very alkaline solution that is practically colorless.

NORMAL CONDITIONS FOR THE DETERMINATION

The real purpose of a strength test is to ascertain how much sodium bicarbonate can be neutralized (and its carbonic acid gas liberated) by a given weight of calcium acid phosphate, *when used in leavening breadstuffs*.

Such a test should therefore be conducted under conditions as nearly as possible like those prevailing in the practical operation of baking.

Some of these conditions are very lucidly set forth by Catlin in the paper referred to and there are one or two others that we may consider, which are never widely departed from in the practical baking operation.

1—Acid phosphate and sodium bicarbonate are simultaneously present in equivalent or approximately equivalent quantities. There is *never* the condition of an excess of sodium hydroxide. Hence, indirect titration wherein a considerable excess of sodium hydroxide is added and boiled with the assay brings about an entirely abnormal condition, tending to produce more basic end-products than simple neutralization.

2—Catlin has shown that in practical baking each gram of acid phosphate has available for reaction purposes about 45 cc. of water as a maximum and probably actually considerably less. Hence excessive dilution is an abnormal condition, nor should such excessive dilution be brought about indirectly by the expedient of using extremely dilute standard solutions. The end-point is at best vague, and there is no excuse for using anything weaker than 0.5 or 0.3 N solutions.

3—Catlin has shown that in practical baking, exposure to a boiling temperature (100° C.) lasts for about 1 min. only. Therefore if boiling is employed at all it should not last over 1 min., and of course in no case should it ever occur in the presence of an excess of caustic soda.

4—Apart from the mineral constituents of the flour no salts are present in practical baking other than the acid phosphate and the bicarbonate, except a small amount of common salt. Hence it is quite inadmissible to add to the assay any substance other than the standard alkali solution (and indicator) unless it be common salt in amount not exceeding one-half of the weight of phosphate under assay. One proposed method calls for the use of an enormous excess of common salt in the assay, which is, of course, inexcusable.

These conditions of actual baking practice can hardly be disputed. How can they be most nearly approximated in an analytical method? In the writer's opinion they are more nearly met by simple, direct titration, using about 30 cc. of water per g. of acid phosphate and employing standard alkali of approximately 0.5 N strength so as to avoid excessive dilution.

The major part of the alkali should be added quickly, but with vigorous stirring to prevent occlusion in the precipitate. The indicator (phenolphthalein) should be present in *liberal* amount so that adsorption by the precipitate does not render the end reaction invisible.

It is hard to imagine that any chemist sincerely believes that a mixture of insoluble calcium phosphates and disodium phosphate which exhibits a markedly alkaline reaction to phenolphthalein is still capable of liberating carbonic acid from carbonates.

AN INACCURATE METHOD

There was recently submitted to the writer a "Method for Determining the Neutralizing Value of Monocalcium Phosphate," said to be used by the chemists of the Agricultural Department of one of the states, and by a number of other chemists, and which "they had found to be the *best*." As it is somewhat typical it is worth reproducing verbatim.

> Weigh into a No. 3A casserole 0.8401 g. of phosphate. Add 25 cc. of cold water and stir. Then run in 90 cc. of 0.1 N caustic soda solution from buret, bring to boil and boil 1 min. Add one small drop of phenolphthalein and titrate back with 0.1 N hydrochloric acid solution. The amount of hydrochloric acid required to cause the pink of the phenolphthalein to just disappear taken from 90 cc. of alkali used gives the neutralizing value of the phosphate in terms of sodium bicarbonate and is expressed in units.
>
> *Extreme care must be exercised in the amount of indicator used. We have found the most satisfactory results by using one drop.* [The italics are the present writer's.]

It may safely be said that the above method is wrong wherever it is specific.

Without any desire to be captious in criticism, it is utterly absurd to weigh to the fourth place in such tests. The end-point is at best vague, and indeterminate within 0.2 cc. of 0.5 N alkali (the writer makes this statement after years of experience and possessing an eye perhaps more than ordinarily sensitive to color changes).

The dilution is about two and one-half times what would occur in baking practice, and the alkali used is more than 30 per cent in excess of the neutralizing power of the phosphate. The instructions are to boil the test at this extreme dilution and in the presence of the huge excess of caustic soda, both conditions that tend to the production of abnormally basic end-products.

But the real scientific gem of the method appears in the instruction to add "one small drop" of phenolphthalein. If a sample of acid phosphate be titrated, following the above method precisely, and if more phenolphthalein be added at the completion of the test, the assay will immediately turn dark red, indicating strong alkalinity, and very considerably more acid will be required to discharge the color again. In fact, if sufficient indicator be used, the final result will approach the simple direct titration, although still somewhat higher, owing to the abnormally basic condition brought about by boiling with excess of caustic solution.

Now there is no escape from the fact that a test conducted according to this method was really very strongly alkaline at the point taken as the end-point, and that this alkaline condition was not evident, simply because insufficient indicator was present, and this with deliberate intent to obtain what is rather naively described as "the most satisfactory" result. It is quite manifest that "most satisfactory" means "highest possible" and nothing else.

There is not the least sanction either in sense or science for the prescribed limitation of the amount of indicator, and there can be no doubt whatsoever that this method of determining the "strength" of acid phosphates gives results about 15 per cent in excess of the true neutralizing value.

If acid phosphates are used with the proportion of bicarbonate of soda as indicated by this test, the resulting products must be strongly alkaline. It is an undoubted fact that acid phosphates *are* used in practice in the proportions indicated, and usually without serious results. In fact, an alkaline condition in breadstuffs may be desirable under some circumstances. But the business of the chemist is solely to report the true neutralizing value of the sample, irrespective of what limiting proportions *may* be used without provoking actual disaster.

Cream of tartar will neutralize sodium bicarbonate in the ratio of 100 to 44.6. There is not the slightest doubt that fairly satisfactory bread can be made using cream of tartar on a basis of 100 to 50, but this would not in the least justify the chemist in reporting cream of tartar as having this neutralizing strength.

DETERMINATION OF CORRECT VALUE

The titration of phosphoric acid, especially in combination with calcium, is necessarily indefinite for several reasons. The end-products are amphoteric in their action on indicators; for instance, they will at one and the same time turn red litmus blue and blue litmus red. This phenomenon is probably a result of the tendency to hydrolysis, especially on dilution or heating, as, for instance

$$Na_2HPO_4 + 2H_2O \rightleftharpoons NaH_2PO_4 + NaOH.$$

Lastly, the end-products may be considerably more basic than dicalcium phosphate if suitable conditions are provided.

As might be expected, considerable work has been done in the attempt to prove conclusively what is the true working value of acid phosphates, and not a little of such work by the writer or under his direction. While he is entirely convinced as a result of his experience, he recognizes the extreme difficulty of furnishing apodictic proof.

A rather conclusive test, devised and worked out by Mr. A. L. Konwiser, formerly assistant to the writer, is perhaps best described by recounting the procedure of an actual series of tests.

A sample of acid phosphate gave a neutralizing value of 69.7 by direct titration. The same sample, titrated precisely in accordance with the "Agricultural Station Method" quoted above, gave a strength of 80+.

A mixture (baking powder) was prepared from C. P. cream of tartar and sodium bicarbonate in exact stoichiometrical proportions, *i. e.*, 100 to 44.65. This was designated as No. 1 and constituted a standard of neutrality or control. Similar mixtures were prepared with the acid phosphate and bicarbonate in the proportions of 100:70, 100:75, and 100:80, and numbered 2, 3, and 4, respectively. All these mixtures were weighed upon a chemical balance to insure accuracy.

Biscuits were made with the four powders, using only flour, water, the leavening powders, and salt. The biscuits were baked side by side in the same oven and when "done" were split open and spotted with specially purified and carefully neutralized litmus solution (purple).

The following results were observed:

SAMPLE	RESULTS
1	The purple color of the litmus was unchanged
2	Color purple but markedly bluer than Sample 1
3	Immediate full blue color. Alkaline
4	Same as Sample 3. No increase in blueness

The acid phosphate used on the 100 : 70 basis (that is practically the indication of the simple direct titration) yields a biscuit that, while very slightly alkaline as compared with the strictly neutral cream of tartar biscuit, is still, for all practical purposes, neutral.

The acid phosphate used on the 75 basis gives a completely alkaline reaction, and the intensity of the blue color is not increased when the acid is used on the 80 basis. In other words, the excess of soda on the basis of 75 is already so large that further excess does not change the color of the indicator.

The biscuits were submitted to a tasting test by an observer who knew nothing whatever of their make-up. This observer pronounced Nos. 3 and 4 "soapy" (that is, alkaline), and in the case of No. 4 the verdict was rendered with grimaces of distaste.

The final conclusion is that 70 (practically the indication of the simple direct titration) is about the correct working strength and is indeed at the upper limit at which it should be used; 75 is too high and gives an alkaline product, while 80 (the indication of the "Agricultural Station Method") is very much too high.

CONCLUSION

When one method of testing a substance gives results 15 per cent or more higher than another method, it naturally leads to embarrassing situations. As long as one manufacturer calls his product 75, 80, 85, or any other strength and can persuade his customers that he is correct, with or without the backing of chemists, official or other, his competitor must do likewise or lose business. But this does not appear to the writer to justify a chemist in reporting a neutralizing strength which he is perfectly sure is greatly in excess of the truth, nor can he salve his conscience by adopting methods that are manifestly devised for the purpose of giving high results.

The writer understands that an effort is on foot to bring about a standardization of the methods of testing acid phosphates—presumably a method sanctioned by the Association of Official Agricultural Chemists. In the very nature of the case absolute accuracy cannot be expected, but it is not difficult to outline a simple method, the indications of which, when applied in practice, will result in neutral or substantially neutral residues in food products.

The Determination of Moisture in Insulating Oils[1,2]

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Many methods of determining water in oils have appeared in the literature, but no reliable simple method has come to the author's notice. By examination of the literature in detail, a classification of methods has been made. This classification includes five qualitative, a dozen approximate, and few quantitative methods. In dealing with moisture in insulating oils, a method cannot be called quantitative unless an accuracy of closer than 0.002 per cent is obtained. The approximate methods include those which determine moisture content to an accuracy of 0.01 to 0.05 per cent. The qualitative tests are those which have been recommended here and there for the use of the electrical engineer as a rapid means of finding the presence of water. No insulating oil should be allowed to take up enough moisture to show positive tests by qualitative methods, because the dielectric strength of an oil becomes less considerably before the moisture can be thus detected.

QUALITATIVE TESTS

1—Addition of anhydrous $CuSO_4$. Turns blue with H_2O.,[1,2,*]

2—Hot nail "spits," indicating H_2O.[1,2]

3—Addition of certain water-soluble, but oil-insoluble dyes.[3]

4—Centrifugation.[4]

5—Electrical precipitation.[5]

APPROXIMATE ANALYSIS

1—Loss of weight by heating. For nonvolatile oils and greases.[6,13]

2—Diluting with solvent and settling by gravity. Applicable to thin oils, but a diluent is to be avoided. Centrifugation may be used to hasten.[7]

3—Use of color comparator tube.[6]

4—Treating with normal acids.[6]

5—Treating with CaC_2. This is convenient, but with petroleums accurate to 3 per cent of the H_2O value only, as C_2H_2 is absorbed by them. The 3 per cent accuracy holds only above 0.01 per cent content.[8]

6—Treating with sodium. One cc. H_2 represents 0.0016 g. H_2O in the sample used. This is accurate and convenient. Complicated apparatus necessary to insure thorough contact of sodium with oil and to eliminate quantitatively all of the hydrogen.[6]

7—Distilling with a immiscible liquid. Water-saturated xylene, a mixture of xylene and toluene, or benzene and toluene are used. Accurate to approximately 0.033 g. of H_2O per 100 cc. of distillate.[6]

8—Directly distilling off the water. This is accurate to within 0.03 per cent, and does not apply to light oils.[6] Inert gases used to dry oils.[2]

9—Water in oils may be tested by conductivity providing no other decomposition products are present. Only approximate results obtainable.[9]

10—Oil mixture with organic solvent to produce cloud. A more general case than No. 7.

11—The Tyndall effect is used to determine finely divided water in suspension.

QUANTITATIVE METHODS

1—By special application of No. 3 (qualitative tests) less than 0.003 per cent H_2O can be detected. Necessitates color scale, clear oils—standardization for quantitative work.

2—Vacuum treatment while shaking sample, heating, and collecting H_2O in P_2O_5 tube. Method quantitative if oil is free from nitrogenous volatile compounds, as is usually the case. By special method we are able to determine water to ±0.001 per cent.

3—Same treatment as No. 2, using freezing mixture to collect H_2O and volatile components, afterwards estimating water by No. 4 method. Good results obtainable, but complicated apparatus must be employed.

4—Vacuum treatment of thin film of oil running over heated surface. Vapor eliminated and measured by oil-water vapor pressure difference.

5—Mixing oil with dry ether (solvent), treating with CaC_2, drawing off C_2H_2 by vacuum, precipitating out in alcoholic $AgNO_3$ solution and noting change in resistance with precipitation of silver acetylide.[8] This gives time-rate curve and is very desirable where both hygroscopic and constitution moisture are involved. It is accurate to less than 0.01 per cent and is chiefly applicable to certain insulating materials and oils.

Inasmuch as the dielectric strength of an oil is greatly influenced by the moisture present,[10] it is highly desirable to determine the moisture content accurately. The different forms in which the moisture is present within the oil may vary greatly. This is dependent upon the composition of the oil and its impurities. Water may be in finely divided suspension, condensed nuclearly upon dust particles, absorbed by fibers or soaps, in colloidal form or in true solution. The true dielectric strength of pure oil is most strongly influenced by water in solution, but the usual conductivity takes place by the alignment of particles within the oil.

Very pure mineral oil of the paraffin series does not dissolve more than 3×10^{-4} per cent H_2O.[11] The unusually high percentage of moisture sometimes found in oils is attracted by impurities which are soluble in oil. Such impurities (unsaturated compounds, fatty acids, etc.) possess a greater coefficient of solubility for water than do the pure paraffins.

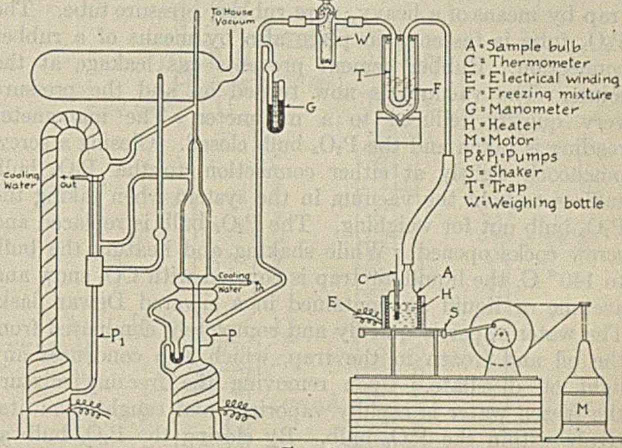

FIG. 1

Of the numerous possible methods of determination of water in transformer and similar oils only two or three may be depended upon for the accuracy desired. A modification of Method 2 (Quantitative Methods) has given excellent results.

PRINCIPLE OF METHOD

Water is fractionated from the oil at reduced pressure and elevated temperature, during rapid agitation of the sample. Under these conditions the partial pressures of oil and water are far apart and fractionation is rapid. The water is collected with some oil distillate in a trap cooled by liquid air. Redistillation of the water and collection in a P_2O_5 weighing bottle take place upon the removal of liquid air. The small amount of oil vapor distilling over passes on through the phosphorus pentoxide. The method depends for its success upon the production of a great number of thin films within the oil sample. A low freezing mixture may be substituted for the liquid air.

APPARATUS AND PROCEDURE

Fig. 1 shows diagrammatically the arrangement of the apparatus. The weighing bulb* is of special design consisting of two glass parts, an inner and outer chamber. The inner chamber (2 cm. in diameter × 10 cm. long) is slightly constricted at the lower end and has a stopcock handle at the upper end. This fits concentrically within the outer chamber (2.5 cm. in diameter × 10 cm. long), and is made airtight by the ground joint near the top. An inlet allows gas to enter the outer chamber first. The gas passes down-

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[1] Presented before the Section of Petroleum Chemistry at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

[2] Published as Scientific Paper 92 of the Westinghouse Electric and Manufacturing Company.

* Numbers refer to Bibliography.

* Modification of bulb used by Dr. H. C. P. Weber, Westinghouse Electric and Manufacturing Company.

ward through the outer chamber, entering the inner from the bottom. Pure P_2O_5 packed between two plugs of glass wool within the central chamber is used as the moisture absorbent. The gas passes up through the P_2O_5 and out through a small tube directly opposite the inlet. By turning the inner member through 90° the bulb is sealed to any gas pressure difference. Such a bulb holds a vacuum many weeks.

The sample bulb, which fits within the heater shaker, is of about 50-cc. capacity. A tube, closed at the bottom and just large enough to accommodate a small thermometer (range 0° to 150° C.), passes down into the bulb. The bulb can be kept at any desired temperature by the electric heater surrounding it. The motor speed can be controlled so that the shaker runs from 50 to 250 per minute. The liquid air trap consists of a closely bent U-tube of 1-cm. tubing, surrounded by a Dewar flask containing liquid air.

PROCEDURE—Before making a run the apparatus is thoroughly cleaned and dried. A few cc. of oil to be tested are used to rinse the sample bulb before pipetting in the 25 to 40 cc. of the oil. The bulb is connected to the liquid air trap by means of a heavy, pure rubber, pressure tube. The P_2O_5 tube is fastened in place also by means of a rubber connection. Rubber cement prevents gas leakage at the joints. The vacuum is now turned on and the pressure very quickly reduced to a millimeter. The manometer reading is taken and the P_2O_5 bulb closed. Closing a screw pinchcock tightly at either connection to the P_2O_5 bulb suffices to hold the vacuum in the system when taking the P_2O_5 bulb out for weighing. The P_2O_5 bulb is replaced and screw cocks opened. While shaking and heating the bulb to 140° C. the liquid air trap is covered with CO_2 snow and acetone or liquid air contained in a silvered Dewar flask. The water vapor is quickly and completely eliminated from the oil and frozen in the trap, which also condenses any light oil distillate. Upon removing the freezing mixture the frozen water is rapidly vaporized and caught quantitatively within the P_2O_5 bulb. By closing the P_2O_5 bulb at the same pressure as in the blank weighing one can readily obtain the eliminated water by difference. Phosphorus pentoxide does not absorb any oil vapors at the pressures used.

Two methods of procedure may be followed. The more rapid method does not account entirely for the moisture in the air within any part of the apparatus. As shown in Table I, it gives comparatively good results, varying ±0.002 from the mean. A single determination is not to be recommended where the best accuracy is desired.

TABLE I

Water Added Per cent	Water Found Per cent	Difference
0.0042	0.0047	+0.0005
0.0194	0.0216	+0.0022
0.0110	0.0092	—0.0018
0.0088	0.0078	—0.001
0.0074	0.0086	+0.0012

$$\sqrt{d_1 + d_2, \text{etc.}} = 0.0012$$

In this case the vacuum is cracked without shaking the sample bottle, thus taking out the air above the oil sample when the weighing tube or freezing mixture is not yet in place. A pinchcock is immediately closed. The freezing mixture is then raised around the trap and the weighing tube put in place, and the determination is made as described above.

The second method of procedure takes into account the amount of moisture in the air. Two blank runs are first made to determine the humidity. Several runs made for humidity moisture check the theoretical values. With the addition of this correction to the first procedure, the moisture in hydrocarbon oils may be determined accurately.

NOTES ON THE METHOD

In determining the moisture content to ±0.001 care must be exercised at every point in the determination. The oil sample must be representative of that which is to be examined. Any apparatus used in connection with the oil should be carefully cleaned and dried and then rinsed with some of the oil sample. Humidity changes influence the water content appreciably if the sample is open to the air. Care should be exercised in keeping the breath away from the sample, as surface condensation of water vapor may greatly influence the result.* The time of a run should not exceed 20 min. This gives ample time to insure complete elimination of the moisture.

Factors which give high results, and hence are additive, may be briefly summarized as follows:

1—Surface condensation of water from humid air.
2—Contamination of any of the apparatus by water or dust.
3—Volatile nitrogenous and basic substances within the oil.
4—External leaks of any kind.
5—Increase of pressure during run so that excess gas is trapped in P_2O_5 bulb.
6—Adsorption of some oil vapor in weighing bulb.

Subtractive errors are as follows:

1—Elimination of water not complete as a result of high viscosity of oil sample.
2—Bath temperature too low.
3—Shaking not vigorous enough to expose all the oil to thin film condition.
4—Decrease in pressure over the initial pressure within the bulb.
5—Time of shaking oil too brief.

Weighing errors may be positive or negative.

Using the representative transformer oil little difficulty is experienced in the determination of water due to its viscosity, impurities present, or to the volatility of the sample. Leaks are readily taken care of by using rubber cement between the glass-rubber connections. Other possible leaks are prevented by proper construction of apparatus. Freshly sublimed P_2O_5 free from organic matter will not absorb and hold any oil under low vacuum conditions. Should any oil distillate come over in appreciable quantities it is readily eliminated by surrounding the P_2O_5 tube by a temperature bath of 100° to 150° C.[12] Though the possible errors seem numerous, it is only necessary to recognize them to eliminate them by following out carefully the procedure recommended, and little difficulty will be experienced in obtaining an accurate result.

BIBLIOGRAPHY

1—*Elect. Club J.*, U. S. A., May **1904.**
2—*Elect.*, **66** (1911), 490.
3—A. H. Gill, "Oil Analysis," 6th Ed., **1913**, p. 22.
4—*Chem.-Ztg.*, **33** (1909), 1259.
5—Bureau of Mines, *Technical Paper* **25** (1912). See also patent literature.
6—*Orig. Com. 8th Intern. Congr. Applied Chem.*, **10**, 17.
7—*J. Ind. Eng. Chem.*, **10** (1918), 357; Direccion General de Mines, Buenos Aires, Bol. **3B** (1915).
8—U. S. Dept. Agriculture, Bureau of Chemistry, *Circular* **97**; *J. Soc. Chem.*, **29** (1910), 197; *Chem.-Ztg.*, **6** (1892), 29.
9—*J. Soc. Leather Chem.*, **3**, 101–4; **14**, 654–74; **3**, 206–8; *J. Ind. Eng. Chem.*, **12** (1920), 486–98.
10—*Elect.*, **66**, 490; *Elect. J.*, **16**, 74–6.
11—See also *Elect.*, **82**, 103, 67, 818; *Z. anorg. Chem.*, **81**, 24–39; *Z. Elektrochem.*, **17**, 348.
12—*Z. anorg. Chem.*, **81**, 24–39.
13—*J. Soc. Chem. Ind.*, **39** (1920), 305.

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* The rubber connections used in the vacuum line do not give up any appreciable amount of moisture after having been once subjected to low vacuum, if care is taken subsequently to keep out humid atmosphere.

A committee of eleven has been appointed to draft tentative plans for an organization of oil men, to comprise refiners, jobbers, producers, supply and tank men, which it is expected will embrace the entire oil industry of the southwest, probably with headquarters in Kansas City. Part of the plan includes the formation of an arbitration board to settle differences between conflicting interests, and an oil exposition to be held yearly.

Method for the Determination of Free and Combined Carbon Dioxide[1]

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In the course of work on the analysis of mine water, it has been found that the ordinary titrimetric methods for the determination of carbon dioxide fail with acid waters. In fact, readings by the standard phenolphthalein method, when any reading is possible, give negative results, and in some cases this error is large. Considering also the fact that the titration of free carbon dioxide in alkaline waters leaves much to be desired, another means than the ordinary titration with alkali was sought.

Reference may be made here to the work of Swanson and Hulett[2] and of Van Slyke[3] and to the apparatus of Van Slyke for the determination of certain constituents of the blood, among then carbon dioxide. The Van Slyke apparatus, however, cannot be directly applied to the analysis of carbonates in general with facility.

A combination of the principles of Dr. Van Slyke and of the nitrometer has solved the difficulty and resulted in the development of the present apparatus.

Apparatus

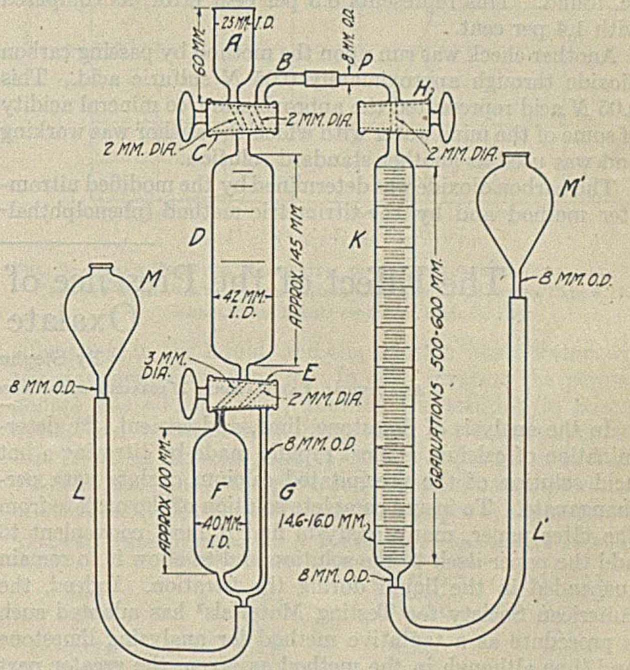
The apparatus consists of a reaction bulb, D, of about 200-cc. capacity, calibrated from the top downward to indicate 10-, 25-, 50-, and 100-cc. capacities. At the upper end it is connected with a 2-way stopcock, C, carefully ground so as to be vacuum-tight when greased. C connects with a cup, A, of approximately 25-cc. capacity, and with a large capillary tube, B, bent at right angles. The lower end of D is connected to a 2-way stopcock, E. This stopcock connects at one outlet with the tube G, and at the other with the bulb F, of about 125-cc. capacity. At the other end the bulb F joins the tube G, and through a hose connection is joined by means of rubber pressure tubing, L, to the mercury reservoir M, of about 500-cc. capacity. K is a gas measuring buret of ordinary type used in nitrometer work and is calibrated from 0 cc. to 100 cc. in 0.2-cc. intervals.

The stopcock and seats are carefully cleaned and greased, B and P connected with pressure tubing, the train filled with mercury and tested under vacuum for air leaks, giving special attention to C and E. The apparatus is now ready for the analysis.

Analysis

The sample is introduced into D from A by means of stopcock C. It may be measured previously by a pipet or buret into A, or it may be measured by drawing into D to the desired calibration. The latter method is sometimes desirable when analyzing a sample containing free carbon dioxide in large amount. By means of a 2-hole rubber stopper with inlet and outlet tube fitted into the top of A, a portion of the liquid to be analyzed may be used to fill and flush out A, thus assuring no mechanical loss of carbon dioxide during the introduction of the sample. If free carbon dioxide alone is desired no acid is added at this point, but if total carbon dioxide is required concentrated sulfuric acid is added by means of cup A and stopcock C till in distinct excess. D is then agitated to mix the water and acid thoroughly, and any gas formed is passed over into K, allowing none of the liquid to pass out of D. The mercury level in K and M is adjusted, stopcock H is closed, and an approximate reading of the gas in K is taken, temporarily disregarding the gas in the capillary. The reservoir M is then lowered and the mercury is drawn from D through the tube G, tending to form a Torricelli vacuum in D. When most of the mercury has been drawn from D, the stopcock E is turned so as to deliver into bulb F. The rest of the mercury and the sample are completely drawn from D into F. E is then closed, imprisoning the sample in F. M is raised and E is turned so as to connect G with D. The mercury will then rise in D. The gas liberated by the evacuation may then be passed over into K and an approximate reading taken, noting the increase.

M is again lowered and most of the mercury drawn from D through G. When D has been nearly emptied, M is raised and E turned so as to permit the sample to pass from F to D. In doing so it is converted into a fine stream which is flattened against the sides of the glass and agitated by the mercury in such a manner that a large surface is exposed to the vacuum in D, thus aiding the liberation of dissolved gas. M is again lowered, the sample imprisoned in F and the mercury are allowed to flow back through G to D, and any gas is passed over into K, and the increase noted. The evacuations are continued till the increase has become negligible. Three to four evacuations are usually required. The gas in the capillary is then displaced with mercury and the gas volume in K read, with the usual precautions taken for such readings. The temperature and pressure are of course noted and corrections made accordingly. If the gas is not dry when the volume is read, correction for moisture must also be made.



A determination can be made with this apparatus in from 15 to 30 min., and a maximum of 3 per cent of error is indicated, though a higher degree of accuracy is usually obtained.

This method was checked in various ways. The exact amount of carbon dioxide present in a sodium bicarbonate solution of approximately 0.5 *N* strength was determined gravimetrically with barium hydroxide. This proved to be 10.142 g. of CO_2 per liter, which is equivalent to 5.14 cc. of CO_2 (at 0° C. and 760 mm.) per cc. of solution. In running the tests with this solution, varying amounts of sample were taken and varying concentrations of acid were used. Table I shows results obtained with this solution:

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[1] Received July 26, 1921.

[2] *J. Am. Chem. Soc.*, **37** (1915), 2490.

[3] *J. Biol. Chem.*, **30** (1917), 347.

Table I

Cc. of Sample Taken	Conc. Sulfuric Acid Used Cc.	—CO_2 at 0° C. and 760 Mm.— in Sample Cc.	Found Cc.	Error Per cent
1.94	20	9.98	9.71	2.7
1.94	20	9.98	9.8	1.8
10	..	51.4	51.3	0.19
10	15	51.4	49.9	2.7
10	Slightly acidified	51.4	50.5	1.75

Certain of the above-measured gas volumes were passed into caustic and showed practically complete absorption. In addition, a 25-cc. portion of the bicarbonate solution was evacuated without acidifying. A reading of 1.7 cc. was obtained, equivalent to a blank of 0.068 cc. of gas per 1 cc. of sample or slightly less than 1.4 per cent of error. When, however, we consider that a part of this blank was undoubtedly due to a decomposition of the bicarbonate under very greatly reduced pressure the error approaches the vanishing point. In this connection, 25 cc. of ordinary distilled water were acidified and evacuated and a reading of less than 0.4 cc. found. This represents 0.3 per cent error, as compared with 1.4 per cent.

Another check was run upon the method by passing carbon dioxide through approximately 0.05 *N* sulfuric acid. This 0.05 *N* acid represented the approximate free mineral acidity of some of the mine water with which the author was working and was used as another standard solution.

The carbon dioxide was determined by the modified nitrometer method and by the titrimetric method (phenolphthalein cold—phenolphthalein hot) using 0.1 *N* sodium hydroxide. The sample was allowed to stand in the laboratory in a large, poorly stoppered bottle for 6 hrs., and again analyzed by both methods.

Table II shows the results obtained:

Table II

	Carbon Dioxide P. p. m.
10 : 00 A. M.	
Titration	402
Gasometric	422[1]
4 : 00 P. M.	
Titration	354
Gasometric	381[1]

[1] Caustic absorption practically complete.

Since the prevailing tendency of the gasometric method is, under these conditions, low, the above figures, while hardly conclusive, indicate that the growing opinion against phenolphthalein as an indicator in carbon dioxide titrations is well founded. Numerous other determinations were made which gave logical, consistent figures.

It is believed that the apparatus as outlined can be conveniently adapted to field work. It was not found necessary to assemble the apparatus for this purpose, but the matter has been given some consideration for possible future use. There appear to be no difficulties that cannot be readily overcome. Care will be taken to standardize properly the dimensions of the apparatus.

The Effect of the Presence of Filter Paper on Permanganate-Oxalate Titrations[1]

By Stephen G. Simpson

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In the analysis of limestone, lime, and cement, the determination of calcium is most rapidly made by titrating a hot acid solution of the precipitated calcium oxalate with permanganate. To insure complete solution of the oxalate from the filter paper, many analysts find it most convenient to add the paper itself to the solution and to allow it to remain suspended in the liquid during the titration. Indeed, the American Society for Testing Materials[2] has adopted such a procedure as a tentative method for analyzing limestone and lime although in the method as given, the greater part of the calcium oxalate is washed from the filter paper with hot water and the paper containing the remainder of the oxalate[3] is added to the solution near the end of the titration. Several textbooks give essentially the same procedure.[4] The fact that permanganate may be reduced by filter paper shreds is generally known, and Myhill[5] has recently emphasized this point in connection with permanganate titrations. For this reason, Gooch[6] filters the calcium oxalate upon asbestos, and others[7] dissolve from the filter paper by means of prolonged washing with hot, dilute sulfuric acid. The extent of this reduction under the conditions of ordinary volumetric titrations is not given, however, and whether or not the effect is great enough to affect appreciably the accuracy of ordinary analytical results is not generally known.

Experimental Details

In the following experiments 0.1 *N* solutions of oxalic acid and potassium permanganate were used, and all titrations were made by means of weighing burets. The ratio of permanganate to oxalic acid was repeatedly established during each series of experiments, and in all determinations the end-point was taken as a faint pink remaining permanent for at least 15 sec. The filter papers were Baker and Adamson's 9-cm. washed papers weighing approximately 0.45 g. each. Since the extent of disintegration and hence the reducing power of the filter paper could not be accurately controlled, it could hardly be expected that the results obtained under apparently similar conditions would be in perfect agreement, but the values obtained checked closely enough to give a fairly accurate idea of the extent of reduction in each case.

The first and second series of titrations were carried out with the object of determining under varying conditions of time and concentration the extent of reduction of an excess of permanganate when kept in contact with filter paper. In the first series, 60 drops (4.6 cc.) of 0.1 *N* $KMnO_4$ were added from a weighing buret to 350 cc. of water containing 20 cc. of 6 *N* H_2SO_4 and heated to 70° C. A filter paper was submerged in the solution and allowed to remain for a

Table I—Reduction of 0.1 *N* Potassium Permanganate by Filter Paper, Varying Time of Contact

Vol. $KMnO_4$ = 4.6 cc. Vol. soln. = 350 cc. Conc. $KMnO_4$ = 0.042 g./l.

Time of Contact Min.	Total Vol. $H_2C_2O_4$ Cc.	Total Vol. $KMnO_4$ Cc.	$KMnO_4$ Equivalent to $H_2C_2O_4$[1] Cc.	Vol. 0.1 *N* $KMnO_4$ Reduced Cc.
1	4.38	4.71	4.57	0.14
1	4.59	4.95	4.79	0.16
1	4.40	4.76	4.60	0.16
3	4.23	4.67	4.42	0.25
3	4.37	4.79	4.56	0.23
3	4.57	5.02	4.77	0.25
7	4.20	4.72	4.38	0.34
7	4.10	4.62	4.28	0.34
7	4.18	4.73	4.37	0.36
20	4.06	4.75	4.24	0.51
20	4.20	4.86	4.38	0.48
20	4.48	5.19	4.68	0.51

[1] Ratio = 1.044.

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[1] Received July 5, 1921.

[2] *Proc. Am. Soc. Testing Materials*, **20** (1920), 632.

[3] Hot water will not remove all the calcium oxalate from the paper. See U. S. Geological Survey, *Bulletin* **700**, 147.

[4] Low, "Technical Methods of Ore Analysis;" Cheever-Smith, "Select Methods in Quantitative Analysis."

[5] *Chem. Age* (*London*), **4** (1921), 151.

[6] Gooch, "Methods in Chemical Analysis."

[7] Sutton, "Volumetric Analysis;" Treadwell-Hall, "Analytical Chemistry," II.

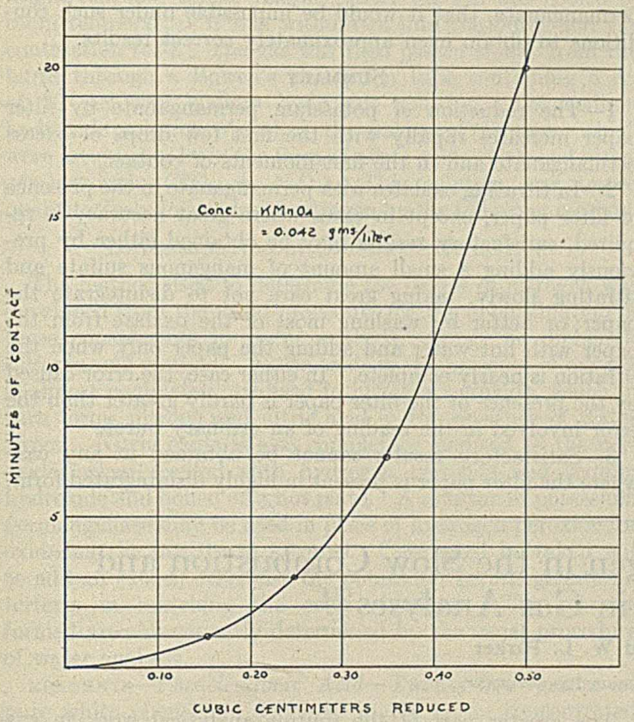

FIG. 1—GRAPH SHOWING REDUCTION OF POTASSIUM PERMANGANATE BY CONTACT WITH FILTER PAPER UNDER CONDITIONS GIVEN IN TABLE I. RESULTS IN TERMS OF 0.1 *N* $KMnO_4$

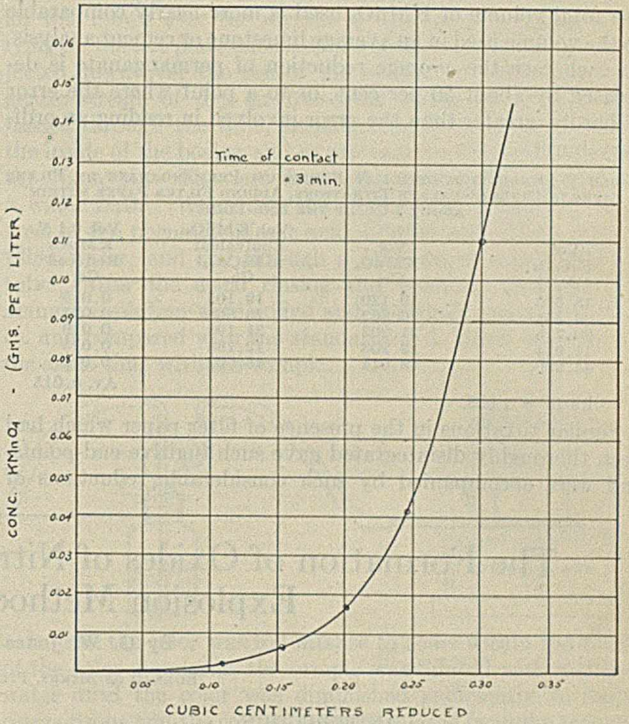

FIG. 2—GRAPH SHOWING REDUCTION OF POTASSIUM PERMANGANATE BY CONTACT WITH FILTER PAPER UNDER CONDITIONS GIVEN IN TABLE II. RESULTS IN TERMS OF 0.1 *N* $KMnO_4$

specified length of time, during which the solution was occasionally stirred and the paper allowed to disintegrate only of its own accord. An excess of the standard oxalic acid was quickly added and the titration was finished with the permanganate. The volume of permanganate used up by the filter paper was calculated in each case in terms of 0.1 *N* $KMnO_4$, and the values obtained are given in Table I. Similar titrations were made keeping the time of contact with the filter paper constant and varying the concentration of the excess permanganate. The numerical results of this series in terms of 0.1 *N* $KMnO_4$ are given in Table II. Figs. 1 and 2 show in graphic form the averages of the results given in Tables I and II. From these graphs it is seen that the reduction of permanganate by filter paper increases very rapidly with the first few drops of excess permanganate and in the first few moments of contact—facts which in themselves show the danger of titrating with permanganate in the presence of filter paper.

TABLE II—REDUCTION OF 0.1 *N* POTASSIUM PERMANGANATE BY FILTER PAPER, VARYING CONCENTRATION OF EXCESS PERMANGANATE

Time of Contact = 3 Min.

Vol. $KMnO_4$ Cc.	Vol. Soln. Cc.	Conc. $KMnO_4$ G./L.	Total Vol. $H_2C_2O_4$ Cc.	Total Vol. $KMnO_4$ Cc.	Vol. $KMnO_4$ Equivalent to $H_2C_2O_4$[1] Cc.	Vol. 0.1 *N* $KMnO_4$ Reduced Cc.
0.24	350	0.0022	0.49	0.62	0.51	0.11
0.24	350	0.0022	0.20	0.32	0.21	0.11
0.24	350	0.0022	0.26	0.38	0.27	0.11
0.77	350	0.0070	0.92	1.11	0.96	0.15
0.77	350	0.0070	0.76	0.95	0.79	0.16
0.77	350	0.0070	0.77	0.96	0.81	0.15
1.9	350	0.017	1.75	2.03	1.83	0.20
1.9	350	0.017	1.72	2.02	1.80	0.22
1.9	350	0.017	2.20	2.48	2.29	0.19
4.6	350	0.042	4.23	4.67	4.42	0.25
4.6	350	0.042	4.37	4.79	4.56	0.23
4.6	350	0.042	4.57	5.02	4.77	0.25
4.6	125	0.110	4.26	4.74	4.44	0.30
4.6	125	0.110	5.24	5.78	5.47	0.31
4.6	125	0.110	4.19	4.67	4.38	0.29

[1] Ratio = 1.044.

In the third series of titrations, 200 cc. of water containing 20 cc. of 6 *N* H_2SO_4 were heated to 70° C., standard oxalic acid was added from a weighing buret, a filter paper was submerged in the liquid, and the solution was titrated with the standard permanganate. In each titration the permanganate was added slowly, allowing the solution to become decolorized between each drop, and the filter paper was broken up as little as possible. The results given in Table III show that, under the given conditions, the average volume of 0.1 *N* $KMnO_4$ reduced by the filter paper is about 0.03 cc.

TABLE III—REDUCTION OF 0.1 *N* POTASSIUM PERMANGANATE BY FILTER PAPER IN DIRECT OXALATE TITRATION

Vol. $H_2C_2O_4$ Cc.	Vol. $KMnO_4$ Cc.	Vol. $KMnO_4$ Equivalent to $H_2C_2O_4$[1] Cc.	Vol. 0.1 *N* $KMnO_4$ Reduced Cc.
2.674	2.786	2.758	0.028
2.082	2.176	2.148	0.028
2.569	2.674	2.651	0.023
2.566	2.689	2.647	0.042
2.674	2.790	2.759	0.031
1.979	2.078	2.043	0.035
3.211	3.338	3.313	0.025
4.024	4.176	4.152	0.024
			Av. 0.030

[1] Ratio = 1.032.

As in all permanganate-oxalate titrations, with the first few drops of permanganate the resulting solution is decolorized only very slowly, during which time the permanganate may be very appreciably reduced by any filter paper shreds present. This source of error may be reduced either by adding a few cubic centimeters of manganous sulfate solution previous to the titration, or by adding the filter paper shortly before the completion of the titration as mentioned above. The effect of the previous addition of manganous sulfate is shown in Table IV, and the effect of adding the filter paper late in the titration is shown in Table V where, incidentally,

TABLE IV—REDUCTION OF 0.1 *N* POTASSIUM PERMANGANATE BY FILTER PAPER IN DIRECT OXALATE TITRATIONS, ADDING MANGANOUS SULFATE

Vol. $H_2C_2O_4$ Cc.	Vol. $KMnO_4$ Cc.	Vol. $KMnO_4$ Equivalent to $H_2C_2O_4$[1] Cc.	Vol. 0.1 *N* $KMnO_4$ Reduced Cc.
2.057	2.132	2.122	0.010
3.131	3.249	3.229	0.020
3.628	3.754	3.744	0.010
3.306	3.432	3.411	0.021
3.478	3.605	3.588	0.017
5.225	5.414	5.392	0.022
			Av. 0.017

[1] Ratio = 1.032.

the total volume of $KMnO_4$ used is more nearly comparable to the volume used in an average limestone or cement analysis. In each case the average reduction of permanganate is decreased by about 50 per cent, or to a point where the error is hardly greater than the error involved in reading an ordinary buret.

TABLE V—REDUCTION OF 0.1 *N* POTASSIUM PERMANGANATE BY FILTER PAPER IN DIRECT OXALATE TITRATIONS, ADDING FILTER PAPER WITHIN ABOUT 2 CC. OF THE END-POINT

Vol. $H_2C_2O_4$ Cc.	Vol. $KMnO_4$ Cc.	Vol. $KMnO_4$ Equivalent to $H_2C_2O_4$[1] Cc.	Vol. 0.1 *N* $KMnO_4$ Reduced Cc.
18.675	19.120	19.105	0.015
26.264	26.892	26.868	0.024
20.716	21.203	21.193	0.010
11.914	12.203	12.188	0.015
43.990	45.014	45.002	0.012
			Av. 0.015

[1] Ratio = 1.023.

Similar titrations in the presence of filter paper which had been thoroughly disintegrated gave such fugitive end-points, and were accompanied by such considerable reductions of permanganate, that it would be impossible under such conditions to obtain even approximately correct results.

SUMMARY

1—The reduction of potassium permanganate by filter paper increases rapidly with the first few drops of excess permanganate and in the first moments of contact.

2—In titrating oxalates with permanganate in the presence of filter paper, except in cases where great accuracy is required, satisfactory results may be obtained either by previously adding a small amount of manganous sulfate and titrating slowly, taking great care not to disintegrate the paper; or better by washing most of the oxalate from the paper with hot water and adding the paper only when the titration is nearly complete. In either case, the error caused by the presence of the filter paper is hardly greater than the error involved in the reading of an ordinary buret.

3—Satisfactory results cannot be obtained in any case where the filter paper is present in highly disintegrated form.

The Formation of Oxides of Nitrogen in the Slow Combustion and Explosion Methods in Gas Analyses[1,2,3]

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INTRODUCTION

As a part of its investigation pertaining to a more efficient utilization of the natural resources of the country and greater safety in mining methods, the Bureau of Mines has occasion to make many analyses of gases from mines. These gases vary from samples of mine air taken under good ventilation conditions to those from mine fires and gases after explosion disasters and the like.

The accuracy of analysis is important, and constant endeavor is made to develop better methods and refinements in gas analysis.

This report deals with the production of oxides of nitrogen when gases are analyzed by the slow combustion and explosion methods under the usual conditions of analysis.

PURPOSE OF INVESTIGATION

The question relative to the production of oxides of nitrogen when combustible gases are burned by slow combustion using a glowing platinum spiral, or by explosion using an electric spark, has been much discussed by authorities on gas analyses.

White[4] finds that large errors result when combustible gases are burned by the slow combustion method and attributes these errors to oxides of nitrogen, since tests made with Greiss's reagent give positive results, and concludes that the slow combustion method is unreliable for accurate gas analysis. Dennis,[5] on the other hand, finds that, "when the spiral was heated for 5 min. to a temperature of dull redness in 100 cc. of air, the colorimetric determination of the nitrite that was formed showed that the amount of the oxides of nitrogen produced did not in any case exceed 0.005 cc. and that the volume is usually much less than this." Dennis further states that under the most unusual conditions the volume of oxides of nitrogen formed was less than 0.01 cc., which in technical gas analysis is inappreciable.

The greater part of the routine analytical work in gas analysis at the Pittsburgh Experiment Station of the U. S. Bureau of Mines consists in the analysis of samples of gases from metal and coal mines. The percentages of total combustibles in these samples are very low, in most cases less than 0.2 of one per cent. For this work gas apparatus of the Haldane type as modified by Burrell[1] is used.

Haldane apparatus is so constructed that volumes can be read to an accuracy of about 0.002 cc. It has a limit of accuracy of about 0.02 per cent when the three combustible gases, methane, carbon monoxide, and hydrogen, are present.

In this method the combustibles are burned with a platinum spiral heated to a bright yellow. It is evident that if appreciable amounts of oxides of nitrogen are formed this method cannot be used since contractions would be produced even when combustibles were absent. When normal air is passed into the slow combustion pipet and the spiral heated to a bright yellow for 3 min., the contraction produced seldom exceeds 0.005 cc. and in most cases is found to be less than 0.002 cc.

To prove or disprove whether these small contractions were due to oxides of nitrogen, ten different platinum wires of No. 28 B & S gage were investigated under conditions as used in analysis.

The wires, 2.25 in. long and wound into a spiral as used in gas analysis, were heated for different periods of time, and at different temperatures, and the resulting gases analyzed for oxides of nitrogen by the method to be described. The greater number of the tests were made with normal air containing no combustible since this condition more nearly approximates the condition in actual use.

OXIDES OF NITROGEN BY THE SLOW COMBUSTION METHOD

The procedure of making the tests was essentially as follows: The platinum wire to be tested having been assembled in the combustion pipet of the Haldane apparatus, about 20 cc. of laboratory air were drawn into the buret and accurately measured, then passed into the KOH pipet and the carbon dioxide removed. The gas volume was again read, passed into the combustion pipet, and burned for a determined

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[1] Received August 3, 1921.

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

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

[4] "The Oxidation of Nitrogen as a Source of Error in the Estimation of Hydrogen and Methane," *J. Am. Chem. Soc.*, **23** (1901), 476.

[5] "Gas Analysis," **1913**, 152.

[1] G. A. Burrell and F. M. Seibert, U. S. Bureau of Mines, *Bulletin* **42**, "The Sampling and Analyses of Mine Gases and Natural Gas."

length of time, at a temperature designated as dull red, bright red, and bright yellow. After the gas was cooled to room temperature it was withdrawn into the buret and the contraction read. The gas was then passed slowly from the buret through a Bowen's absorption tube containing 5 cc. of 10 per cent sodium hydroxide solution. The sodium hydroxide solution absorbed the oxides of nitrogen which were assumed to be in the form of nitric oxide (NO) and nitrogen peroxide ($NO_2 + N_2O_4$). This solution was tested quantitatively for oxides of nitrogen by the following method.

DETERMINATION OF OXIDES OF NITROGEN

The method used to determine the oxides of nitrogen was developed from the usual procedure for the determination of these constituents in water analysis,[1] using the diphenylsulfonic acid method. Nitric oxide in the presence of oxygen is almost completely oxidized to nitrogen peroxide, which in turn forms nitrous and nitric acid in the presence of water vapor. Nitric oxide is also completely oxidized to the peroxide[2] when treated with hydrogen peroxide and sodium hydroxide and boiled on a hot plate. A solution of potassium permanganate may be used in place of hydrogen peroxide for oxidizing the nitrites to nitrates. Care must be taken not to add an excess, otherwise the potassium permanganate interferes in matching the color standards. The nitrates formed are subsequently determined by the usual procedure of water analysis.

REAGENTS—*Phenolsulfonic Acid*—Twenty-five grams of pure white phenol are dissolved in 150 cc. of concentrated sulfuric acid, 75 cc. of fuming sulfuric acid (15 per cent SO_3) are added, stirred, and the mixture is heated for 2 hrs. at 100° C.

Standard Nitrate Solution—A solution is made containing 0.72 g. of potassium nitrate per liter. Ten cc. of this solution are evaporated on a water bath until about one drop is left and the remaining water removed with a current of dry air. The residue is thoroughly moistened with 2 cc. of the phenoldisulfonic acid solution and made up to 1 liter. One cc. of this solution equals 0.001 mg. of nitrogen.

Sodium Hydroxide—A 10 per cent solution of chemically pure sodium hydroxide is used.

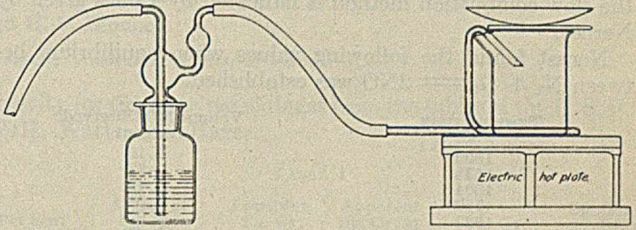
Ammonium Hydroxide Solution—Equal parts of concentrated ammonium hydroxide and distilled water are used.

PREPARATION OF STANDARDS—A set of standards was made by measuring the required amounts of the standard potassium nitrate into Nessler tubes, adding 5 cc. of ammonium hydroxide solution and diluting each to 100 cc. with distilled water.

The standards had the following values:

Standard No.	Standard KNO_3 Solution Cc.	Value of Standard Cc. NO_2 at 0° C. and 760 Mm. Hg
1	0	0.0000
2	1	0.0018
3	2	0.0035
4	4	0.0070
5	7	0.0133
6	10	0.0176
7	15	0.0263
8	20	0.0355
9	25	0.0438
10	30	0.0525
11	35	0.0613
12	40	0.0700

PROCEDURE—After the oxides of nitrogen were taken up by the sodium hydroxide solution, this solution was transferred to an evaporating dish, 5 cc. of hydrogen peroxide were added, and it was allowed to stand 30 min. The solution was evaporated almost to dryness on a hot plate, then completely on a water bath. The evaporation was hastened by an arrangement shown in the figure, whereby heated dry air was blown over the surface of the liquid. A glass tube lying on the hot plate encircled the beaker, then rose and projected down over the rim of the beaker for about 1 in. A gentle stream of dry air free from oxides of nitrogen was passed through the tube, keeping a small excess pressure on the inside of the beaker and so prevented contamination from the room air. The last final evaporation was finished on a water bath. When dry the residue was moistened with 2 cc. of the phenoldisulfonic acid, diluted with 10 cc. of distilled water, and run through a filter paper into a Nessler tube. After the usual rinsing and washing, 15 cc. of the ammonia solution were added and the whole made up to 100 cc. and compared with the standards. A blank was run at the same time with the sample.



In case the color was too intense to come within the range of the color standards, the sample was diluted with distilled water until the color was diminished sufficiently to make comparisons and the correct value calculated from the amount of dilution.

RESULTS OF TESTS

Table I gives the results obtained by testing different platinum wires. Nos. 1 to 7, inclusive, were ordinary grades of platinum wire sold for combustion purposes. No. 8 con-

TABLE I—CC. OF OXIDES OF NITROGEN PRODUCED BY DIFFERENT PLATINUM WIRES WHEN HEATED FOR DIFFERENT LENGTHS OF TIME AND DIFFERENT TEMPERATURES
(Oxides of nitrogen reported as NO_2—20 cc. of gas used in each test)

TEST No.	Time of Burning, Min.	Temp. of Wire[1]	Contraction of Gas Due to Burning, Cc.	Blank NO_2 of Solutions, Cc.	NO_2 Found, Cc.	NO_2 Produced, Cc.	REMARKS
1-A-3	3	A	0.008	0.004	0.007	0.003	Laboratory air
1-A-2	2	A	0.005	0.004	0.005	0.001	Laboratory air
1-A-1	1	A	0.000	0.004	0.005	0.001	Laboratory air
1-B-3	3	B	0.000	0.004	0.004	0.000	Laboratory air
1-B-2	2	B	0.004	0.004	0.004	0.000	Laboratory air
1-B-1	1	B	0.001	0.004	0.004	0.000	Laboratory air
1-C-3	3	C	0.000	0.004	0.004	0.000	Laboratory air
1-C-2	2	C	0.000	0.004	0.004	0.000	Laboratory air
1-C-1	1	C	0.002	0.004	0.004	0.000	Laboratory air
2-A-3	3	A	0.003	0.004	0.004	0.000	Laboratory air
2-A-2	2	A	0.002	0.004	0.004	0.000	Laboratory air
2-B-3	3	B	0.000	0.004	0.004	0.000	Laboratory air
2-C-3	3	C	0.000	0.004	0.004	0.000	Laboratory air
3-A-3	3	A	0.009	0.004	0.004	0.000	Laboratory air
3-A-2	2	A	0.003	0.004	0.004	0.000	Laboratory air
3-B-3	3	B	0.004	0.004	0.004	0.000	Laboratory air
3-B-2	2	B	0.000	0.004	0.004	0.000	Laboratory air
3-C-3	3	C	0.000	0.004	0.004	0.000	Laboratory air
4-A-3	3	A	0.000	0.004	0.004	0.000	Laboratory air
4-B-3	3	B	0.000	0.004	0.004	0.000	Laboratory air
5-A-3	3	A	0.006	0.002	0.003	0.001	Laboratory air
5-A-1	1	A	.....	0.002	0.002	0.000	2 per cent CH_4 and air mixture
5-B-3	3	B	0.005	0.002	0.002	0.000	Laboratory air
6-A-3	3	A	0.003	0.002	0.004	0.002	Laboratory air
6-B-3	3	B	0.008	0.002	0.001	0.001	Laboratory air
7-A-3	3	A	0.002	0.002	0.002	0.000	Laboratory air
7-A-12	12	A	0.007	0.002	0.005	0.003	Laboratory air
8-A-3	3	A	0.002	0.005	0.006	0.001	Laboratory air
8-B-3	3	B	.....	0.005	0.006	0.001	Laboratory air
8-C-2	2	C	0.000	0.005	0.005	0.000	Laboratory air
8-A-2	2	A	.....	0.005	0.006	0.001	2 per cent CH_4 and air mixture
9-A-3	3	A	0.004	0.005	0.006	0.001	Laboratory air
9-A-2	2	A	.....	0.005	0.005	0.000	Laboratory air
9-B-3	3	B	0.000	0.003	0.006	0.001	Laboratory air
9-B-1	1	B	0.000	0.005	0.005	0.000	Laboratory air
9-B-2	2	B	.....	0.005	0.006	0.001	2 per cent CH_4 and air mixture
10-A-2	2	A	0.004	0.005	0.005	0.000	Laboratory air
10-B-3	3	B	0.000	0.005	0.005	0.000	Laboratory air

[1] A = bright yellow; B = bright red; C = dull red.

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[1] "Standard Methods of Water Analysis," American Public Health Association, **1917**, 3rd Ed., 23.

[2] R. R. Tatlock and R. T. Thompson, "The Analysis of Waters and Their Changes in Composition When Employed in Steam Raising," *J. Soc. Chem. Ind.*, **23** (1914), 428.

tained a small amount (less than 5 per cent) of iridium. No. 9 was platinum gauze, containing 10 per cent palladium gauze. No. 10 was pure palladium gauze.

Each wire was tested at the different temperatures and the different lengths of time given in the table. The contractions produced on burning the total oxides of nitrogen and the net oxides of nitrogen after subtracting the blank are given.

From the table it is seen that the maximum quantity of oxides of nitrogen produced was only 0.003 cc., a value within the experimental error for routine gas analysis. This quantity was produced by using a bright yellow heat and burning for 3 min.

In the greater majority of tests, the oxides of nitrogen were found to be zero.

That little if any oxides of nitrogen should be produced by the slow combustion method is indicated by values given by Nernst.[1]

Nernst found the following values when equilibrium between $N_2 + O_2 \rightleftharpoons 2NO$ was established.

TEMPERATURE ° C.	Volume NO Observed Per cent
1500	0.10
1538	0.37
1604	0.42
1760	0.64
1922	0.97
2000	1.20
2500	2.60
3000	5.30

The time required to form one-half the concentration of NO at equilibrium conditions from air is given by Jellinek[2] as follows:

Absolute Temperature ° C.	Time of Formation of Half the Possible Concentration of NO from Air
1000	81.62 yrs.
1500	1.26 days
1900	2.08 min.
2100	5.06 sec.

Taking 1500° C., the highest temperature at which the platinum wire is used (platinum melts at 1733°), it would require a longer time than 3 min. (the maximum time a wire is used in most gas analysis) to produce one-half the concentration as given above, providing there is no catalytic effect due to the platinum wire. Since, according to the values given by Nernst, only 0.10 per cent NO is produced at 1500° C., the amount of oxides of nitrogen at 1500° C. would not be over 0.05 per cent with burnings of 3-min. duration.

To supplement the values obtained in Table I where mostly laboratory air was used in the tests, three tests were made on an Orsat apparatus with larger amounts of combustibles. The presence of combustibles were suggested as being favorable for the production of oxides of nitrogen.

The results are given below:

Test No.	Gas	Gas Cc.	Air Cc.	O_2 Cc.	Blank NO_2	Total NO_2	NO_2 Obtained Cc.
1	H_2	5.5	92.5	0.0	0.005	0.005	0.000
2	H_2	12.6	85.2	0.0	0.005	0.005	0.000
3	CH_4	20.1	41.5	41.5	0.005	0.005	0.000

Wire heated to a bright yellow.

This table shows that no oxides of nitrogen are produced when combustibles are burned in air, or mixtures of oxygen and air, when the wire is heated to a bright yellow, the usual temperature used in slow combustion methods.

OXIDES OF NITROGEN BY THE EXPLOSION METHOD

A series of tests were made for oxides of nitrogen by exploding synthetic gas mixtures in a Morehead buret and examining the residual gases for oxides of nitrogen as previously described. Since water is used in the Morehead buret it was necessary to use distilled water for each test and to change the analytical procedure somewhat.

TABLE II—RESULTS OF TESTS OF OXIDES OF NITROGEN PRODUCED BY THE EXPLOSION METHOD

Test No.	Gases Used for Explosion, Cc.: H_2	CH_4	Air	Oxygen	NO_2 Found Cc.	Blank NO_2 Cc.	Net NO_2 Cc.
1	5.5		92.5	....	0.005	0.005	0.000
2	12.6	....	85.2	....	0.005	0.005	0.000
3	15.2	....	84.2	....	0.005	0.005	0.000
4	25.2	....	75.2	....	0.005	0.005	0.000
5	30.0	....	70.2	....	0.005	0.005	0.000
6	50.2	....	49.3	....	0.005	0.005	0.000
7	59.8	....	39.8	....	0.005	0.005	0.000
8[1]	69.5	....	30.3	....	.....	.....	.....
9	30.0	....	49.6	5.2	0.011	0.005	0.006
10	39.7	....	46.0	14.6	0.050	0.005	0.045
11	49.7	....	26.2	24.9	0.163	0.005	0.158
12	....	8.2	92.0	....	0.005	0.005	0.000
13	....	9.8	89.7	....	0.005	0.005	0.000
14	....	12.2	87.7	....	0.005	0.005	0.000
15	....	14.2	85.8	....	0.005	0.005	0.000
16	....	10.5	80.0	7.5	0.011	0.006	0.005
17	....	10.4	67.9	21.6	0.125	0.005	0.120
18	....	15.0	39.8	25.0	0.150	0.006	0.144
19	....	15.0	50.8	25.2	0.163	0.006	0.157
20	....	14.0	66.0	20.0	0.285	0.005	0.280
21	....	12.9	66.5	20.6	0.350	0.005	0.345
22	16.5	4.7	5.1	23.0	0.200	0.005	0.195

[1] Did not explode.

The different gas mixtures given in Table II were introduced into the buret and measured. After the gases were thoroughly mixed, a spark was passed across the electric terminals and the gases exploded. After the explosion sodium hydroxide solution was added to the buret in small amounts at a time and allowed to stand 1 hr. or more to insure complete absorption of the oxides of nitrogen. All the water and hydroxide solution mixed with the water was then withdrawn and used for the test for oxides of nitrogen.

DISCUSSION OF TABLE II

The results of the tests are given in Table II. The volume of oxides of nitrogen varied from 0 to 0.345 cc. When air was used for the oxygen supply, no oxides of nitrogen were produced when either hydrogen or methane was exploded. The proportions of air to gas were varied from the lower to the upper explosive limit for both hydrogen and methane.

When a mixture of oxygen and air was used for the explosion, varying amounts of oxides of nitrogen were formed depending upon the proportions used.

These tests indicate that oxides of nitrogen are not produced in detectable quantities by the sparks between the terminals, but are rather a result of the flame temperature produced when the gases are exploded. The flame temperature of gas-air mixtures is lower than gas-oxygen mixture, due to the inert nitrogen present in air. In other words, there exists a critical point of flame temperature above which oxides of nitrogen are formed.

That gases should not be analyzed with oxygen by the explosion method is apparent by inspection of Table II. In Test 20, 14 cc. of methane, 66 cc. of air, and 20 cc. of oxygen were used for the explosion, and 0.28 cc. of oxides of nitrogen was produced. This 0.28 cc. produces an error in the results of $\frac{0.28}{14}$, which equals 2 per cent in the final result. This error in the usual gas analysis, where analysis is made for methane and hydrogen, distributes itself between the two values. Some of the oxides of nitrogen produced are partly absorbed by the water before the contraction is read and the rest by the caustic potash.

CONCLUSIONS

1—The production of oxides of nitrogen by the slow combustion method when the time of burning is not more than 3 min. and the wire is not heated beyond a bright yellow is within the experimental error in routine gas analysis. Under the above conditions not more than 0.003 cc. of oxides of nitrogen is produced. The purity of the platinum wire has no effect on the quantity of oxides of nitrogen produced.

2—No oxides of nitrogen were produced by the explosion method when air was used as the oxygen supply.

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[1] *Z. anorg. Chem.*, **49** (1906), 213; *Z. Elecktrochem.*, **12** (1906), 527.

[2] *Z. anorg. Chem.*, **49** (1906), 229.

3—When mixtures of air and oxygen were used as the oxygen supply in the explosion methods, appreciable quantities of oxides of nitrogen were formed which are too large to be disregarded in gas analysis. On a basis of 0.15 cc. of combustibles taken for analysis, the error due to oxides of nitrogen may vary 2 per cent in the calculated results when oxygen-air mixtures are used.

4—The production of oxides of nitrogen by the explosion method is due to the flame temperature developed by the gas mixture when exploded rather than to the sparking across the electrodes.

5—The addition of oxygen raises the flame temperature and reaches a critical point above which oxides of nitrogen are produced in appreciable quantities.

6—The method used for determining the quantity of oxides of nitrogen produced was accurate to 0.001 cc. and was a modification of the diphenolsulfonic acid method used in water analysis for determining oxides of nitrogen.

LABORATORY AND PLANT

Revised Specific Gravity Table for Orthophosphoric Acid at 25°/25° C.[1]

By N. P. Knowlton and H. C. Mounce

Laboratories of the Mallinckrodt Chemical Works, St. Louis, Missouri

In the course of routine analyses in this laboratory, it was very constantly observed that the relation between the strength and specific gravity of orthophosphoric acid, as determined, did not agree with published tables.

All the data available on the strength-specific gravity relation were examined and the figures found in the following sources were plotted for comparison: the 15° and 25° C. tables of the United States Pharmacopeia VIII, a table at 17.5° C. in Hager's Commentary on the German Pharmacopeia, a table at 15.5° C. by J. Watts,[2] and a table by Schiff.[3] When completed, this chart showed some very striking inconsistencies. For instance, the lines representing the tables of the U. S. P. VIII at 15° and 25° C. gave higher specific gravities for a given strength of acid than the tables of Hager, Schiff, and Watts, making due allowance for temperature differences. It was also found that the plotted lines were not uniform, and that the various curves were not parallel, the variations between the tables being much greater at some points than at others. This evident lack of accord in these tables prompted the present attempt to establish more accurately the true relationship between the specific gravity and strength of so important a substance.

Experimental

Orthophosphoric acid of about 90 per cent was purified by two recrystallizations. The various strengths were made by dilution of the crystallized acid with distilled water. Over 100 determinations of various strengths and specific gravities were made, at intervals of about 5 per cent, from 3.39 per cent up to 90.26 per cent. The specific gravity determinations were made in a 50-cc. pycnometer of the Reischauer type, with a neck of about 4-mm. bore. The temperature adjustments were made in a thermostat at 25° C. with a maximum variation of ±0.05° C. All figures represent apparent specific gravities, weighings having been made in air with brass weights. The strength determinations were made by the standard magnesium pyrophosphate gravimetric method. In order to check the accuracy of the method and manipulation, C. P. disodium orthophosphate, after several recrystallizations, was made anhydrous and assayed, using the same procedure as with the phosphoric acid itself. Two independent assays gave 100.05 and 99.97 per cent, respectively. A number of the solutions assayed were submitted to other workers, who independently checked the authors' results.

Table I is a compilation of the results obtained, each in close duplicate, with a maximum error of 0.05 per cent. There are also included the interpolated figures for specific gravity for the same percentages from the tables of the U. S. P. VIII, Watts, and Hager.

Table I

Per cent H_3PO_4 Determined	Apparent Sp. Gr. at 25/25° C. Determined	Apparent Sp. Gr. at 25/25° C. U.S.P. VIII	Apparent Sp. Gr. at 15/15° C. U.S.P. VIII	Sp. Gr. 15.5/15.5° C. J. Watts	Sp. Gr. 17.5/17.5° C. Hager
3.39	1.0187	1.019	1.019	1.018	1.016
5.66	1.0309	1.032	1.032	1.030	1.030
11.23	1.0616	1.064	1.065	1.062	1.063
11.44	1.0637	1.066	1.066	1.063	1.065
17.63	1.1009	1.104	1.105	1.100	1.102
21.55	1.1261	1.129	1.130	1.124	1.128
28.43	1.1715	1.176	1.178	1.170	1.175
31.17	1.1918	1.195	1.197	1.190	1.195
36.53	1.2289	1.235	1.238	1.228	1.233
48.12	1.3189	1.328	1.332	1.315	1.323
51.61	1.3506	1.359	1.362	1.347	1.354
53.23	1.3658	1.374	1.377	1.362	1.367
56.24	1.3911	1.401	1.405	1.391	1.394
61.91	1.4485	1.456	1.460	1.448	1.449
68.62	1.5131	1.524	1.528	.....	1.518
74.45	1.5734	1.586	1.591	.....	1.582
78.72	1.6195	1.634	1.638	.....	1.631
78.87	1.6213	1.636	1.640	.....	1.633
82.82	1.6659	1.681	1.684	.....	1.679
83.62	1.6727	1.690	1.694	.....	1.688
85.62	1.7016	.....	.....	.....	1.712
87.29	1.7188	.....	.....	.....	1.731
89.56	1.7479	.....	.....	.....	1.758
90.26	1.7558	.....	.....	.....	1.766

A computation of all the possible errors entering into these determinations indicates that the apparent specific gravities expressed in Column 2 are correct to within 0.0002 for the lighter acids, while the error for the higher gravities is slightly higher, owing to the difficulty in adjusting the meniscus in a viscous liquid.

This table shows very strikingly that the U. S. P. VIII figures for specific gravity are much higher than those of the other authorities. It will be noted also that Watts' results approximate very closely the authors' figures, when allowance is made for the difference in temperature.

Hager's table agrees rather closely with the authors' at a few points, but varies quite widely at others. The graphs representing these tables, if extended to 100 per cent, practically converge at a specific gravity of 1.8840. It is interesting to note that when actual determinations are reported in the literature the figures do not differ greatly from the authors' results, but that the completed tables show the greatest variations. From this it would seem that the tables have been compiled from a limited number of actual determinations, and that many of the figures represent interpolations or extrapolations.

The graph of our figures forms a perfectly smooth line of very slight, continuous curvature nearly analogous to the plotted line of Watts' table, whereas the curves of the U. S. P. VIII and Hager tables are represented by a number of broken straight lines.

From the plotted curve of our values for the determined

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[1] Received August 8, 1921.

[2] *Chem. News*, **12** (1865), 160.

[3] *Ann.*, **113** (1860), 191.

apparent specific gravity at 25°/25° C. and strength of acid, Table II has been prepared.

TABLE II

Per cent H_3PO_4	Sp. Gr. at 25/25° C.	Per cent H_3PO_4	Sp. Gr. at 25/25° C.	Per cent H_3PO_4	Sp. Gr at 25/25° C.
1	1.005	32	1.197	62	1.449
2	1.011	33	1.205	63	1.457
3	1.016	34	1.212	64	1.467
4	1.022	35	1.219	65	1.477
5	1.027	36	1.226	66	1.486
6	1.033	37	1.233	67	1.496
7	1.038	38	1.241	68	1.506
8	1.044	39	1.249	69	1.516
9	1.049	40	1.256	70	1.527
10	1.055	41	1.264	71	1.537
11	1.060	42	1.271	72	1.547
12	1.066	43	1.279	73	1.558
13	1.073	44	1.286	74	1.569
14	1.079	45	1.294	75	1.579
15	1.085	46	1.302	76	1.589
16	1.091	47	1.310	77	1.600
17	1.097	48	1.318	78	1.611
18	1.103	49	1.327	79	1.622
19	1.110	50	1.336	80	1.633
20	1.116	51	1.345	81	1.644
21	1.123	52	1.354	82	1.655
22	1.129	53	1.363	83	1.667
23	1.135	54	1.372	84	1.678
24	1.142	55	1.381	85	1.690
25	1.149	56	1.390	86	1.702
26	1.155	57	1.399	87	1.715
27	1.162	58	1.409	88	1.728
28	1.169	59	1.419	89	1.740
29	1.176	60	1.429	90	1.753
30	1.183	61	1.439	91	1.766
31	1.190	..	.....	..	.....

A critical examination of all factors entering into this work indicates that, from Table II, the strength of mixtures of pure orthophosphoric acid and water can be calculated to an accuracy of about 0.05 per cent.

Graded Seal for Joining Pyrex to Lead Glass[1]

By W. C. Taylor and Austin Bailey

APPARATUS DIVISION, CORNING GLASS WORKS, CORNING, NEW YORK

In connection with research problems it is often necessary to join together apparatus whose parts are made of different kinds of glass, such as Pyrex, lime, and lead. Since these glasses have entirely different physical constants it is necessary to employ certain intermediate glasses with properties not so widely separated from one another. However, it is desirable to limit the number of glasses used in order to shorten the length of the seal and to decrease the labor required in its production.

Several patents[2] have been granted on methods of sealing quartz to glasses for the purpose of making vacuum-tight seals to leading-in wires.

Commercial graded seals from Pyrex to lead glass have so far been unsuccessful for several reasons. Intermediate glasses formed by mixing definite proportions of these two glasses all contained lead which caused blackening in the flame. Several of these intermediate glasses were subject to very rapid devitrification in heating and were commercially difficult to produce because of this same tendency. The number of such intermediate glasses required for a good seal was at least seven.

The authors have succeeded in developing a seal consisting of five glasses intermediate between Pyrex and lead glass. The glasses are all comparatively stable and can be worked repeatedly without devitrification. All of the intermediate glasses are of a lead-free borosilicate composition which makes the seal suitable to be worked in any ordinary blast lamp.

Of the factors which enter into the production of a satisfactory graded seal, the most important are expansion coefficient, viscosity, and softening point. The softening point is defined as that temperature at which a rod 1 mm. in diameter and 23 cm. long, the upper portion of which is heated in a furnace 15 cm. long, increases in length at the rate of 1 mm. per minute under its own weight. In making this seal the range of the softening point varies from 817° to 623° C. and the linear expansion coefficient varies from 0.0000032 to 0.0000089 per ° C. The smallest differences in expansion coefficient lie between the intermediate glasses and the Pyrex and lead glass, respectively. This smaller difference is necessitated by a large difference in softening point at one end, and a large difference in composition and viscosity at the other.

In making up the graded seal the worker begins at the low expansion (Pyrex) end and after heating up the two consecutive glasses to such a temperature that the viscosities become approximately the same he blows the joint into its finished form. In cooling he partly reheats the lower expansion glass so that on final cooling it will pass through a greater range in temperature and thus approach more nearly the size of its nearest neighbor. He repeats the same operation over and over until the lead glass is finally sealed into place and the graded seal is complete.

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[1] Received July 8, 1921.

[2] U. S. Patents 1,173,688 (February 29, 1916), to Elihu Thomson; 1,014,757 (June 16, 1912), to Keyes and Kraus; 1,191,630 (July 18, 1916), to Weintraub; Brit. Patent 18,300 (November 10, 1913), to British Thomson-Houston Co.

Plan Campaign for Standardization of Biological Stains

A meeting of representatives of scientific organizations, members of the National Research Council and others interested in obtaining and supplying biological stains of standard quality, was held at the Chemists' Club, New York, November 5, 1921. The meeting had been called by Dr. L. R. Jones, chairman of the Division of Biology and Agriculture of the National Research Council, and was presided over by him. The general need for standardized dyes or stains used in preparing and studying specimens in biological laboratories was discussed. It was the consensus of opinion that the standardization would have to be chemical as well as biological. It is a well-known fact that certain samples of methylene blue, for example, give a satisfactorily stained specimen, whereas other samples sold as methylene blue are totally unsatisfactory. The difference may be in the chemical analysis and in the reaction toward certain tissues.

Having agreed upon the general need for standardization, the Conference next turned to the selection of the proper organization or individuals to carry on such standardization. It was suggested that the coöperation of the various Government Bureaus and the National Research Council might be enlisted and their aid, together with the work of the scientists representing individual associations, would soon solve the problem. Representatives of the laboratories of the Department of Agriculture who were present volunteered their services, and the representative of the National Research Council stated that funds would be available for such clerical work as might be required.

In order to begin on a definite program, the Conference finally decided to work on the standardization of methylene blue, eosin, and gentian violet. Chemical analyses of available samples of these dyes will be made, and they will be tested out for efficiency as biological stains by representative zoölogists, bacteriologists, botanists, and scientists in the Color Laboratory of the Department of Agriculture. It is hoped that sufficient progress will have been made by the time of the meeting of the American Association for the Advancement of Science in December, so that standardized samples of these three dyes will be available for distribution and checking by laboratory men throughout the country. The Conference was composed of the following men: Dr. L. R. Jones, chairman, representing the National Research Council; Dr. McClung, representing the zoölogists; Dr. Conn, representing the bacteriologists; Dr. Hazen, representing the botanists; Drs. Ambler and Ball, representing the Department of Agriculture; Mr. H. E. Howe, representing the National Research Council; Mr. R. T. Will, representing the dealers in biological stains; and Mr. Keohan, representing the Chemical Foundation.

The Grasselli Medal of the Society of Chemical Industry is not to be awarded for 1921.

SPECIAL COST FACTORS AND THEIR RELATION TO THE DEVELOPMENT OF OUR ORGANIC CHEMICAL INDUSTRY[1]

By Gaston Du Bois

Monsanto Chemical Works, St. Louis, Missouri

We claim, and rightly so, that the quality of our American dyes is equal to that of German-made dyes, but unfortunately we cannot claim that our costs of production are no higher than the costs of production in Germany. In consequence of these abnormally high costs, we are losing the foreign markets to which we had begun to export our dyestuffs in gradually increasing quantities, as is shown in the 1920 Census of Dyes. From 1917 to 1920 we exported the following amount of dyes, expressed in dollars:

1917........	$ 7,548,963.00
1918........	15,266,520.00
1919........	15,728,499.00
1920........	29,823,591.00

However, during the first four months of 1921 our exports showed a marked decline:

January	$1,292,709.00
February	469,764.00
March	670,281.00
April	365,010.00

More than half of our exports in 1920 went to Asia and South America, but owing to our inability to meet foreign quotations, Germany is now rapidly reconquering these markets.

If we consider that in 1920, 23 per cent of our total production of dyes were exported, we can readily understand that the loss of foreign markets added to the present industrial depression must greatly affect our industry, and even should a majority in Congress understand our situation and decide to enact the necessary legislation to permit the American industry to supply the home demand for dyes, we should bear in mind that we cannot expect to export dyestuffs until we can produce at a competitive cost with Germany. If we are not able to do so, our volume of production must necessarily remain small as compared with the German production, and we shall be compelled to play second fiddle to the German combination.

In 1920 we produced 88,263,776 pounds of dyes, of which roughly 23 per cent were exported; therefore the home consumption amounted to 65 or 70 million pounds, which exceeds the imports of 1914 by 15 to 20 million pounds. The pre-war German production of dyes was in excess of 200,000,000 pounds, that is, more than three times the amount consumed in the United States in 1920, and more than four times the amount imported into the United States in 1914.

We can hope to be a factor in the world dye market only if we are able to produce the most important dyes at a competitive cost with Germany. At the present time our costs of production are two to three times higher than in Germany. If a certain dye is produced in Germany at a cost of 50 cents per pound, this same dye will cost here from $1.00 to $1.50 to produce and in some cases our cost will even exceed this ratio.

Some of the factors contributing to our high costs are well understood, and may simply be referred to here as:

1—Wages and salaries, which are to-day about seven times higher in the United States than in Germany.

2—Volume of production, which is inferior in the United States to that in Germany.

3—Yields and experience, which we can concede are generally superior in German plants producing dyes for thirty to forty years.

Five Important Factors

There are, however, some other important factors influencing costs which are not generally fully recognized, and the importance of which is frequently not fully appreciated even by a great majority of dye chemists and others responsible for the development of our dye industry, and it is to these special features which affect our costs that I wish to call your attention. These items, which are often included in "overheads," are:

Depreciation
Obsolescence
Idle plant cost
Insurance
Taxes

A study of these various items of cost leads us to the realization that, even though the war is over, its effect is still felt in these five items of cost fully as heavily as at any time since 1917. Raw material prices, labor, coal, and other items of cost have dropped during the past year, but the high costs at which our dye plants were built during the war are bound to reflect on present costs of manufacture, owing to these five items.

How little consideration is given to these points by the average chemist can best be seen by the manner in which he will estimate the cost of manufacture of some intermediate or dye. We frequently hear the wildest statements made, in all good faith, regarding cost figures. There is an element of danger to our industry in such ill-advised statements, inasmuch as frequently the hope of realizing profits will induce individuals to undertake the manufacture of a product, and the attempt may result in failure and consequent loss. The most highly trained and intelligent chemist, if not fully familiar by years of experience with actual cost calculations, is more liable greatly to underestimate a cost than he is to overestimate it.

It may be of interest to recall here one of the useful and constructive activities of the American Dyes Institute. In 1919 a Committee of Cost Accountants was appointed by the American Dyes Institute for the purpose of formulating uniform cost accounting methods, and the report of this Committee was made and printed in a most interesting pamphlet in February 1920. To quote from this pamphlet:

> One of the most difficult and important questions to be considered in the dye and chemical industry is the proper application of depreciation, obsolescence and maintenance as elements of cost.
>
> In the dye industry obsolescence assumes a position of paramount importance in relation to costs, and it is essential to have a clear understanding of what is contemplated by the term and a sufficiently high rate set to cover obsolescence as charged against costs to fit the needs of the industry.
>
> Obsolescence means the loss of value of buildings and equipment or other assets, which become useless or partly so by reason of causes other than wear and tear or accident. Some observers feel that an obsolescence charge may be as high as 35 to 40 per cent of the value of the equipment, and in some cases even more, but a very conservative average would be 20 to 25 per cent.

Obsolescence—Obsolescence is an item of cost which is more frequently overlooked than any other and which, therefore, is frequently responsible for failures and inability to pay out dividends. It is this very point which is so frequently overlooked by chemists in general, who recommend the purchase of equipment and expenditures for erecting a plant for the manufacture of an intermediate or dye based on estimates of cost in which obsolescence is omitted. After operating for two or three years more or less successfully, the owner realizes that he must either give up the manufacture or adopt a better process, of which he had no knowledge when he undertook the manufacture or which may not have existed then. And so it comes about that honest optimists urge others to invest their money, and after this has

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

been done it often happens that an improved process must be adopted and new equipment purchased before the old equipment has been paid for out of the profits of operation. The chemist, in such instances, is frequently totally ignorant of the damage he has caused, and on the contrary is fully convinced of his great efficiency in having in so short a time so materially improved the manufacturing process as to necessitate a complete change of equipment, without thinking for a second that he has been the cause of great financial losses.

This obsolescence cost should be emphasized at this time because our industry is in a period of development necessitating frequent changes in process and equipment to such an extent as to affect our profits materially, whereas Germany has to a great extent gone beyond this period of development and its industry has become far more stabilized.

DEPRECIATION—Depreciation is the decline in value of buildings or equipment such as may reasonably be expected to occur as a result of wear and tear, and is continuous.

Depreciation on buildings in chemical plants may be from 3 to 10 per cent depending on the type of construction. Depreciation on equipment in chemical plants may average from 10 to 20 per cent per year, but may in some instances run as high as 50 per cent.

IDLE PLANT CHARGES—Another very important factor of cost is the increase in cost of manufacture due to stoppage in manufacture, which we will call "idle plant charges." Such a stoppage may be due to fire, improvements or changes in machinery or in process, strikes, accidents, shortage of raw material, decrease in sales, or drop in prices. Interruptions of manufacture are far more frequent than would appear at first sight and are naturally part of the cost of manufacture and can be charged either to overhead or manufacturing expenses depending on circumstances.

INSURANCE AND TAXES are naturally higher to-day than they ever were, and therefore are comparatively important items of cost.

As the result of inflated war values all of the above-described elements of cost are themselves inflated and make up a substantial percentage of cost figures. The writer has had an opportunity to compare the item of depreciation in the cost of manufacture of products which he manufactured prior to 1914 with the corresponding depreciation in 1921. On an average of six products, the depreciation item was in 1921 exactly twice the amount charged in 1914, figured on the same basis of 100-pound production. This increased depreciation resulted from the necessity of rebuilding new plants during the war, either on account of changes in process or of increased demand.

Unwise Duplication of Effort

The subject of costs may be apparently foreign to matters of interest to the Dye Section of the American Chemical Society. Realizing, however, that the future development of the American dye industry is dependent not only on the ability of our research and manufacturing chemists but also on their commonsense and on their ability to take a broad view of the situation, it has seemed to the writer that the question of costs should be of general interest.

It is a fact that we have during the last few years forged ahead in leaps and bounds, we have developed our plants without question or hesitation, we have undertaken the manufacture of innumerable intermediates and dyes without paying very great attention to the activities of our neighbors or competitors, frequently without exact knowledge of the market requirements. It seemed that the possibilities of development knew no limits. Our dyes found a ready market and we increased our plants to supply more goods, which in turn were sold as fast as produced, until all at once we struck a stone wall, and we began to wake up to the reality. The 1920 Dye Census tells us the tale.

Some of the data furnished by the Tariff Commission, showing how many manufacturers have reported the production of the various intermediates and dyes are quoted below:

INTERMEDIATES	NUMBER OF MANUFACTURERS
Acetanilide, technical	9
1-Amino-2-naphthol-4-sulfonic acid	13
1-Amino-8-naphthol-3:6-disulfonic acid	13
p-Aminophenol and hydrochloride	10
Aniline oil	14
Benzaldehyde	8
Benzidine base	9
Benzoic acid, U. S. P. & technical	8
Dimethylaniline	7
Dinitrotoluene	11
2-Naphthol-3:6-disulfonic acid	16
Nitrobenzene (Oil of Mirbane)	9
Nitrosodimethylaniline	11
m-Phenylenediamine	15
Salicylic acid, U. S. P	9
o-Toluidine	8
DYES	
Butter Yellow	9
Alizarin Yellow GG	11
Alizarin Yellow R	10
Orange II	12
Fast Red A	12
Salicine Black U	14
Agalma Black 10 B	16
Bismarck Brown	11
Benzo Blue 2 B	14
Benzopurpurine 4 B	11
Direct Deep Black E W	14
Magenta (or Fuchsine)	12
Methyl Violet	9
Alkali Blue	10
Sulfur Black	12
Sulfur Blue	9
Sulfur Brown	15
Sulfur Green	10
Eosin Lakes	31
Lithol Red	26
Red Lakes	35

A word to the wise is sufficient. The Tariff Commission has said the word and now the question arises: Are we wise? Are we going to organize our industry in such a way as to eliminate unnecessary duplication of effort. Are we going to concentrate our energies on doing a few things *well* or are we going to attempt *each of us* to manufacture all the chemicals we need, independently of whether we do so efficiently or not?

Have not our manufacturing plants up to this day, and some of our large plants in particular, adopted the policy that their salvation depends on their ability to manufacture all crudes, intermediates and dyes, rather than to permit others to supply one or the other of the intermediates required? We would be far better off if one small manufacturer produced all the *p*-nitroaniline required by our industry than if this product were manufactured independently by three large concerns as the tail end of their plants, because the small manufacturer will give his only product more attention and will probably operate more efficiently, and can serve several large plants at one time.

As an illustration of the various points referred to, the following table, taken from actual manufacturing figures, shows the various items of cost in the production of a fairly important intermediate.

This table illustrates a plant designed to produce 1,200,000 pounds of the intermediate. It is seen that the indirect manufacturing expenses, which include obsolescence, depreciation, etc., amount to 18 per cent of the total cost of the product. Let us assume that a second plant decides to take up the manufacture of this same intermediate, aiming to supply the full market requirements. After some more or less unpleasant experiences and losses, this new manufacturer succeeds in supplying one-half of the demand and therefore produces 600,000 pounds yearly. What is the result? The cost of production of both manufacturers is now 47.68 cents instead of 40 cents per pound, because both plants are working at one-half capacity and the indirect expenses have increased from 18 to 30 per cent of the total cost. If two other manufacturers plan to obtain for themselves the full market the result may be that all four manufacturers will be producing, and therefore the cost of production will increase to 54.59 cents, the indirect expenses having increased to 40 per cent of the total cost.

	Total Cost	I. Cost per Lb. Cents		II Cost per Lb. Cents		III Cost per Lb. Cents	
Production, pounds		1,200,000		600,000		300,000	
Raw materials	$248,420	20.71		20.71		20.71	
Direct mfg. expense	108,620	9.00		9.00		9.00	
Rent taxes, insurance	9,120	0.76		1.62		2.28	
Depreciation, 15 per cent	30,000	2.50		5.00		7.50	
Obsolescence, 15 per cent	30,000	2.50	X_1	5.00	X_2	7.50	X_3
Interest, 6 per cent	12,000	1.00		2.00		3.00	
Other indirect expense	6,000	0.50		0.75		1.00	
General admin. expense	7,920	0.66		0.66		0.66	
Selling and shipping	35,640	2.97		3.00		3.00	
		40.00		47.68		54.59	

Indirect Expense

X_1— 7.26 cents, 18 per cent of total cost
X_2—14.27 cents, 30 per cent of total cost
X_3—21.28 cents, 40 per cent of total cost

It may appear that this is an exaggeration, but it is a characteristic illustration of what has happened frequently in this country during the last few years. We have in the United States three manufacturers with a producing capacity of over 2,000,000 pounds of the intermediate referred to in the above illustration and a consumption of less than 600,000 pounds yearly; yet a fourth large manufacturer is seriously contemplating taking up the manufacture of this article. You no doubt realize that our industry is overexpanded in many lines. If it must live on the domestic trade alone, it is high time that we call a halt and begin considering our industry as a whole and not only certain individual units.

There are men with brains, there is energy and determination in every large organization in our industry, and no one organization can claim to monopolize these essentials for success. Our efforts should be directed toward coördination in our industry, for some day we shall face a competitor who knows coördination and elimination of ruinous duplication. If we do not learn our lesson now, our industry will unquestionably suffer later.

Summary

1—We are unable to meet German competition as to costs and are therefore rapidly losing our foreign trade in coal-tar chemicals.

2—Contributing to high costs, outside of wages and other well-understood elements, are other factors such as obsolescence and depreciation, idle plant charges, etc., which are not usually sufficiently recognized by most chemists but which are to-day important items of costs because they are necessarily still figured on the basis of high war values.

3—We have to-day much duplication of effort in our organic chemical industry which still further adds to the burden of these indirect expenses. The consequence of duplication is overexpansion, inasmuch as we attempt to operate four plants where two could take care of our requirements. This condition doubles the depreciation, obsolescence, and idle plant charges.

If such are the existing conditions, what is the remedy?

Much can be said in discussion of what we should do, but it is needless at this time to discuss details which can be easily worked out, provided we recognize the necessity of a change in policy.

What we need is a different mental attitude. We must stop spreading out horizontally and instead we must dig deep down to establish better foundations. This new mental attitude which we must adopt is one of effective coöperation between American manufacturers, and it is necessary that chemists themselves adopt this mental attitude of coöperation, as they are and must be dominating factors in shaping the future of chemical industry of this country. By our intelligent advice and interest, manufacturers will be assisted in abandoning our war-time methods and will adopt a healthier plan of development, taking into consideration, first of all, the needs of our national industry. Instead of encroaching on fields already fully covered in order to satisfy local conditions or personal ambitions, the chemist can, where there is a desire to expand, lead the way towards virgin or neglected fields, of which there are still so many in this country. By so doing you will have done your bit towards minimizing a serious evil threatening our industry.

SOCIAL INDUSTRIAL RELATIONS

Food and Shelter

By H. W. Jordan
Syracuse, N. Y.

Food and shelter absorb from 70 to 90 per cent of the living expense of 85 millions of our 100 million people. Food originates from agriculture. Shelter, which is clothing, housing, and furniture, is in large part textiles, wood, and leather grown from the land.

As wages and salaries are consumed mainly to provide these essentials of life, the most effective way to maintain low cost production in the chemical and engineering industries, and in all industry, is to secure low cost production and distribution of these primary essentials while maintaining equable profit to producers and distributors of them. Maintenance of efficient agriculture and forestry is infinitely more necessary to engineering industry than a tariff.

The extraordinary growth of the United States was founded on free land, cheap food, and ample shelter. Present social discontent and spread of confiscatory ideas spring from increasing cost of food and shelter. Distress of city unemployment is intensified by complete separation of the great majority of our people from direct contact with the land, and their consequent inability to provide food and shelter by their individual labor at the very source of these necessaries of life.

In the period of village or small city industry, a depression in manufacture was not serious. The surplus workers went back automatically to the farms where there was plenty food, fuel, and housing. The normal reaction of depression that followed the Civil War was readjusted by flow of the unemployed to the Eastern farms and the free lands of the West. Little money was in circulation, but there was plenty food, fuel, and shelter back home on the farm.

In 1921, with a large proportion of manual and mental workers city born, with no home ties in the country whatever, and with money from wages or salary the only means of getting the essentials of life, the industrial worker, whether machine tender or chemist, soon becomes resentful when unemployed. He finds himself a product and victim of a complex economic system which caught him young and taught him only one or two narrow, special ways of earning his living. His condition is a result of applied science and of modern, specialized industrial efficiency.

THE LAW OF SPECIALIZATION IS AT WORK UPON HIM. Extreme specialization has led to such lack of adaptability that his chances of survival are greatly diminished unless he returns to a more generalized type. Accordingly, in many cases, he reverts to the primitive occupation of buying and selling. But he stays in the city, because the country offers no appeal to him.

HOUSING IS AN EXAMPLE OF THE ACTION OF MODERN INDUSTRY. New England, New York, Michigan and all the industrial states had extensive timber areas fifty years ago, from which lumber was produced every winter in such abundance that a substantial house to shelter a family of five or six could be built for $2500 from lumber that grew within ox haul. Wood for home fuel was equally cheap and plentiful. Building lots cost little, because free land in the West held down the price of all land.

In 1921 such a home costs $5000 to $8000 chiefly because Eastern lands are stripped of forests, and lumber for houses comes from Oregon, Arkansas, or Georgia. The freight on it is more than the cost of the dressed lumber at the Oregon sawmills. Our annual freight bill on lumber from distant sources exceeds half a billion dollars. Wood for domestic fuel is not to be had at all. Home wood lots are as extinct as the buffalo. Building lots have multiplied in price.

SIMILAR CONDITIONS PREVAIL WITH FOOD. City industrial competition has so depleted farm labor that we no longer feed ourselves from nearby land. We import a substantial percentage of beef, wheat, and corn from Argentina and Canada, mutton from New Zealand, butter and cheese from Denmark, potatoes from Scotland, eggs from China, wool from Australia, lumber, pulpwood, and paper stock from Canada and Norway.

Butter, cheese, eggs and other dairy products used to constitute 30 per cent of our food. Now they are only 15 per cent. Although they are the most nutritious and essential foods, and can be produced within motor truck distance of our industrial cities in plenty, they have been replaced by white flour and sugar foods and by tropical fats and fruit that sustain long haul freight charges often in excess of their cost where they are grown. Declining use of dairy foods and excessive consumption of sugar and white flour is a main cause of loss of teeth, diabetes and widespread malnutrition of children.

Industrial employment managers deplore the inefficiency of workmen. Chemical operators are driven to distraction by the stupid mistakes of city born workmen. Frantic attempts are made to Americanize foreign born Slavic and Latin laborers by teaching them English, with a lot of patter about American institutions.

All the while industrial management makes no attempt to maintain or restore the single great influence that typified the former self-reliant American of Northern European stock and Anglo-Saxon speech. That influence was direct contact with the land and the production of one's own food by one's own labor; a process that compels the use of all one's wits.

INDUSTRIAL MANAGEMENT DOES NOT REALIZE that extreme specialization in city industry is producing equally extreme social discontent and economic helplessness of the individual because industrial management has evolved no method of coöperation between the land and city industry. Worse yet, industry has so drained the farms of labor that the farmer is forced to pay excessive wages, competitive with city industrial workers. Formerly he had abundant labor of boys and youths raised on the land, who worked for board and clothes, and a small, but adequate money wage. This low cost labor and the free land in the West made food wonderfully cheap, and so abundant that our exports were mainly food.

Agriculture and forestry cannot compete with city wages. They require low cost labor that must be provided through coöperation with city industry.

ANOTHER IMPORTANT FUNCTION OF THE LAND is that when nations shift from rural to city life, to the extent that the country is distressed for labor, and ownership of the land is transferred to non-residents so that farms with their food production are in the hands of tenants or financially cramped owners, those nations decline in social, economic, and moral influence. Religion dies as the people lose the idealism that springs from the land and close contact with nature. Rome fell under that influence.

The industries of applied science that chemists and engineers have created since 1880 are confronted by that condition. Modern industry has drained the land, the source of food and shelter, of its requisite share of manhood. Industry has conducted no research to coördinate the land with city, factory production. It has reared an entire generation of city born workers who know nothing of the land. Industry has cut itself off from its three most essential raw materials; self-reliant manhood, food, and shelter. And industry is burdened almost to collapse by excessive wages, taxation, and public charity costs that are part of the reaction from neglect of the land. The unemployed are on the payroll of industry even though the books show no charges to that account.

SUCCESSFUL INDUSTRIAL MANAGEMENT IN THE TWENTIETH CENTURY will be guided by the fact that the greatest profits to industry come from minimum cost of food and shelter that leave a margin of 40 per cent or more from which to accumulate new capital by personal thrift, and upon which to build and maintain superior standards of living. The superficial and gross public spirit that manifests itself by indifference to secondary education, by decline in the drama and rise in jazz, by mediocrity in political leadership and falling influence of religion is in large part the reaction from high cost food and shelter with too small a reserve for expression of the practical high idealism that differentiated America from other nations—the idealism that made America the biggest and best market in the world for manufactured goods.

Scientific physical and chemical research to evolve great industrial plants, new machines, and new processes has subsided. That early phase of industry is drawing to a close and is becoming routine. The great industrial research problems of the twentieth century must be those of human relations. Foremost among these will be the vital task of coördinating the land and its production of food with the applied science of city industry.

Are there no creative industrial executives, no forward looking men who see this vision? The task must be undertaken by the chemists and engineers to bring out creative leaders and engineering statesmen who will apply science to commerce, economics and government as they have applied it to industry. As Korzybski has said, "Neither engineers nor scientific men have any right to prefer their own personal peace to the happiness of mankind; their place and their duty are in the front line of struggling humanity, not in the unperturbed ranks of those who keep themselves aloof from life."

American Association of Textile Chemists and Colorists

About 150 representative textile chemists and colorists from all parts of the country gathered at Boston during the Textile Exposition, on November 3, and organized the American Association of Textile Chemists and Colorists. The following officers were elected: Professor Louis A. Olney, Lowell Textile School, president; William D. Livermore, American Woolen Co., Lawrence, Mass., and William H. Cady, United States Finishing Co., Providence, R. I., vice presidents; Walter E. Hadley, Clark Thread Co., Newark, N. J., secretary; Winthrop C. Durfee, consulting chemist, Boston, treasurer. The following members of the executive council were chosen: George A. Moran, Pacific Mills, Lawrence, Mass.; Walter M. Scott, Cheney Bros., South Manchester, Conn.; A. E. Hirst, American Printing Co., Fall River, Mass.; Elmer C. Bertolet, Philadelphia Textile School; James L. Amsden, Rockland Finishing Co., Haverstraw, N. Y.; W. K. Robbins, Amoskeag Manufacturing Co., Manchester, N. H.

Local sections of the Association are to be formed shortly, embracing the territory adjacent to Boston, New York, and Philadelphia.

A statement of the objects of the Association was printed on page 891 of the October issue of THIS JOURNAL, in connection with the account of the preliminary meeting in New York City in September.

NOTES AND CORRESPONDENCE

A Study of the Fundamental Laws of Filtration Using Plant-Scale Equipment

Editor of the Journal of Industrial and Engineering Chemistry:

Work of the kind described in the paper of the above title, appearing in THIS JOURNAL, 13 (1921), 610, meets with the decided approval of the writer, but he feels obliged to criticize certain statements and conclusions made as likely to produce incorrect impressions.

In the first place a statement is made that the fundamental law of filtration is expressed by the equation

$$\frac{dV}{d\theta} = \frac{KA^2P^n}{V^m}$$

where V = total volume of liquid filtered; Θ = time; A = filtering area; P = pressure; K = a constant; n = an exponent of P varying with the nature of the solids, and m = a possible exponent of V depending upon the solids.

The writer does not agree with the author here, as no filtration can take place without a filter base, *i. e.*, a porous mass to initiate the process—frequently cloth. In the above equation the effect of the filter base is utterly neglected and it cannot therefore be properly called the fundamental law of filtration. Furthermore, it fails to consider separately the effects of the resistance of the cake, the per cent of solids in the mixture, or the rate of deposition of solids. The effect of these variables are lumped into one constant, K, whereas in a fundamental formula they certainly ought to be separated so that the effect of changing any one of them can be studied.

To show that the formula is not really reflective of actual conditions and hence not fundamental, the writer integrated it, taking $m = 1$ as assumed in the article, obtaining the following expression:

$$V = C\,P^{\frac{n}{2}}\,\theta^{1/2} \qquad C = \text{constant}$$

Next the writer plotted the 55 lb. per sq. in curve shown in Graph 3 on logarithmic cross-section paper. Now if the equation is correct, the slope of the curve ought to be 0.5. Actually, as will be seen in Curve 1, the curve is not 0.5 nor indeed is it even a straight line. Unquestionably this discrepancy from the equation which is called fundamental is due in slight part to error in observation, but primarily because the equation entirely neglects the effect of the filter base, a fundamental condition of filtration, which is a subtractive quantity, as given in the present writer's formula,

$$V = \sqrt{WP\theta + N^2} - N,$$

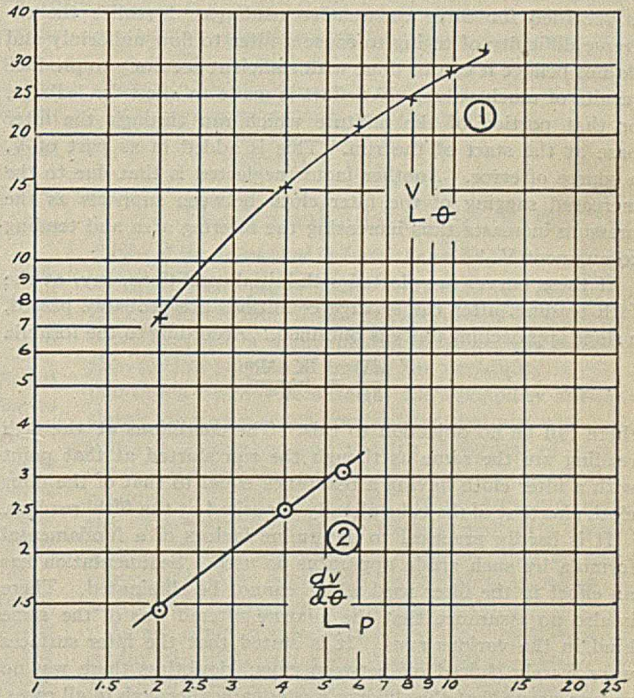
where V = total discharge; P = pressure; $W = \frac{2K}{R\%}$; $N = \frac{KR_m}{R\%}$; Θ = time; K = rate of deposition of solids; R = resistance of the porous mass; % = per cent of solids in the mixture; and R_m = resistance of the filter base.

The effect of the filter base is important and increases in importance as the per cent of solids in the mixture, %, and the resistance of the porous mass, R, decrease, and as the rate of deposition, K, and the resistance of the filter base, R_m, increase.

If a time-discharge curve be obtained from a fine suspension of precipitated calcium carbonate in a liberal amount of water, it will be found that N becomes a very important factor. The writer recalls how puzzling the various curves and slopes of time-discharge curves were until fully explained by the fundamental law of filtration which he later derived, together with the device described in his article appearing in *Met. Chem. Eng.*, 16 (1917), 161.

Baker makes the following statement, referring to the writer's article in *Met. Chem. Eng.*, 15 (1916), 198 (enunciating the fundamental law of filtration): "In the formula which Sperry derives, he takes the exponent of the pressure to be 1.0 in all cases, which, as proved by Lewis and Almy, and by the results described in this article, is entirely erroneous."

That this statement is not true is evident by the last paragraph of my article, referring to the fundamental law of filtration derived in that article, "Two other factors may be added to this list, one, a factor modifying P, the pressure to allow for the squeezing together of nonrigid solids as the pressure increases ......" The fact also that the writer is at the present time, and has been for some time past, doing research work on the effect of pressure on the rate flow of water through nonrigid porous masses, indicates that he was well aware that n was not necessarily unity.



The writer has carefully analyzed the curves shown in Mr. Baker's article, but only after diligent effort, owing to the absence of any log of the observations taken. The conclusion reached that $n = 2$ is in his opinion not correct. Comparison of the constant pressure curves in Graph 3 shows at a glance that this cannot be so. The formula for the total volume as given above is:

$$V = CP^{\frac{n}{2}}\,\theta^{1/2}$$

In other words, if $n = 2$ and the pressure be doubled, the value of V would also double, providing Θ is kept constant. Drawing a perpendicular line through Θ = 64, it is found that for 20 lbs. per sq. in. V = 150 cu. ft., whereas for 40 lbs. per sq. in. V = 180 cu. ft. If the value of n was 2, the latter should be 300 instead of 180.

The writer also drew a horizontal line corresponding to V = 150 cu. ft. At the points where this line intersects the three constant pressure curves there is obviously the same thickness of cake. The only difference at these three points is the pressure and rate of flow corresponding. If at each of these points a tangent be drawn as accurate as conditions permit, the slope of each tangent measures the approximate rate of flow at that point. If these slopes be plotted on logarithmic cross-section paper against the pressure, then the slope of the resulting line is n. This is true according to the formula:

$$\frac{dV}{d\theta} = \frac{KA^2P^n}{V^m}$$

because the tangents correspond to $\frac{dV}{d\theta}$, and $\log \frac{dV}{d\theta} = n \log P + \log \frac{KA^2}{V^m}$, where V = constant and $m = 1$.

In plotting the slopes and pressures, a value of n less than unity is obtained, in the neighborhood of 0.70 (see Curve 2).

Turning to Graph 2 (Baker) where an effort is made to find the value of n which is finally taken as 2, the writer tabulated the data as well as the small scale of the curve would permit. He found that the data were rather inaccurate. The text states that readings were taken every 5 min., and since the curves are for constant flow conditions the difference between consecutive readings ought to be the same. Actually this is far from being the case. Not only is this true, but furthermore the pressure readings are not uniform; in some cases no change in pressure is recorded for three consecutive readings. I realize the extreme difficulty of trying to cause a filter to flow uniformly and do not believe it can be done with sufficient accuracy to produce results of much value. No effort is made to allow for leakage, or that portion of the mixture which ran through the filter base at the start of the run. This is added in as part of V, a source of error. Another factor neglected is that due to the increased sagging of the filter cloth between supports as the pressure increases thus increasing the filtering area and tending to augment V.

If these curves are plotted with initial conditions, say, at the fifth reading, after the leakage conditions are probably passed, a slope approaching unity is obtained. According to the formula

$$\frac{dV}{d\theta} = \frac{KA^2P^n}{V^m}$$

there can be no objection to this. The conditions at the fifth reading are the same as though the run started at that point with a filter cloth having a resistance equal to that of the filter cloth plus that of the cake already deposited at the fifth reading.

It is hardly practical to determine factors of a fundamental formula by such crude apparatus as used. Sedimentation has an effect in the filter used which cannot be eliminated. There is also no assurance that the mixture filtered was of the same kind in the various runs. It is stated that the filter surfaces were merely sluiced off between runs; doubtless there was no way to prove that the sluicing was equally thorough in all cases.

D. R. Sperry

119 McKee St.,
Batavia, Ill.
August 13, 1921

....

Editor of the Journal of Industrial and Engineering Chemistry:

The criticisms in the above letter may be summarized as follows:

1—The filtration law we used is not fundamental because:

(*a*) The resistance of the filter base was not taken into account.

(*b*) It fails to account separately for (1) resistance of cake, (2) the per cent solids in sludge, and (3) the rate of deposition.

(*c*) Because even our own data do not give a straight line whose slope is approximately 0.5 when the log of the volume of discharge is plotted against the log of the pressure.

2—Our quotation from Mr. Sperry's article in *Metallurgical & Chemical Engineering* incorrectly interpreted Mr. Sperry's views.

3—That whereas for the sludge in question we compute n as 2 in the formula

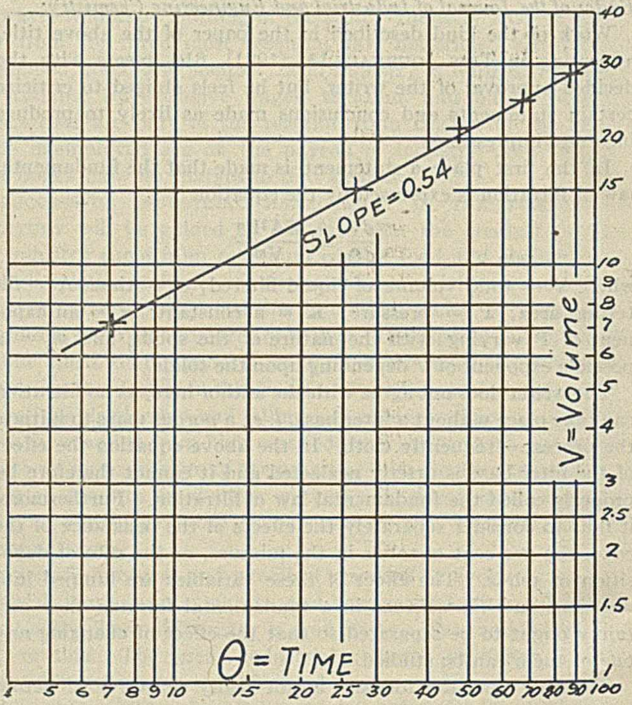
$$\frac{dV}{d\theta} = K \frac{P^n}{V^m},$$

Mr. Sperry computes it as 0.7.

4—That a tabulation made from our log pressure-log volume plot shows $n = 1$.

5—That in general the formula developed by Mr. Sperry is to be preferred to that developed by Lewis and Almy [This Journal, 4 (1912), 258].

6—That it is impractical to develop a fundamental formula with the crude commercial apparatus used.



We will take up these criticisms in the order named.

1—(*a*) The influence of the resistance of the filter base is important, but only as a resistance in series with the filter cake resistance itself. In view of the severe limitations of present filtration formulas we did not believe this refinement necessary at present. Mr. Sperry is right that the ultimate formula should include this term.

(*b*) Our constant "K" contained the three factors in question for our particular sludge. Here, too, these factors should be separated in the final formula.

(*c*) It is obvious, from Graph 1 and the text, that the formula used does not hold during the first few minutes of a run. It is also equally clear from the same graph that after this preliminary period the volume squared is proportional to the time. Therefore, when the log of volume is plotted against log of time (after this preliminary tare time) a straight line with a slope of 0.5 must result. Mr. Sperry, in his plot, tries to show this mathematical relationship to be untrue, but if the points used by Mr. Sperry are replotted after allowing for the initial tare time of 13 min. (intercept of $V^2-\theta$ curve with $V^2 = O$) the conclusion reached from our Graph 1 is confirmed. The plot accompanying this communication is Mr. Sperry's points plotted on the same paper and with the same scales, but with this 13 min. allowed for.

2—The formula quoted from Mr. Sperry's article (*Loc. cit.*) is as follows:

$$dT = \frac{R\%Q}{PT}\, dQ + \frac{R_m}{P}\, dQ$$

Certainly in this formula P has an exponent of 1, and hence the rate $\frac{dQ}{dT}$ must have been assumed to vary with the first power of the pressure. Also, in at least three places in the text of the article Mr. Sperry states that the rate of flow varies with the first power of the pressure, as, for example, on page 201 where it is stated, "for the present the proposition that the rate of flow through a filter cake varies directly as the first power of the pressure and inversely as the first power of the thickness must be accepted as true." That the rate does not vary directly with the pressure is shown by experimental results obtained under careful laboratory conditions and published in This Journal in 1912.

3—If we assume the filtration law used to have the same coefficients in both constant pressure and constant rate runs and if the values of *n* in the different runs gave close checks, then Mr. Sperry's method of computing *n* and ours should agree. However, both of the above assumptions are incorrect. Mr. Sperry's coefficient of $n = 0.7$ applies to the constant pressure runs, whereas our coefficient $n = 2.0$ applies to the constant rate runs. The text referred to $n = 2$ for constant rate runs and the curvesin Graph 2 are labeled "constant rate." Mr. Sperry's method could have been used on the constant rate runs (*i. e.*, for constant thickness of sludge, *v*, plot log $\frac{dV}{d\Theta}$ against *n* log P, the slope of the resulting line giving the value of *n*). When the rates were 158 and 194 cu. ft. per hr., respectively, the points lie too close for accuracy, but even so, this method of calculation indicates *n* at least equal to 2. In our article the value of $\frac{n}{m}$ for each constant rate run was obtained by plotting the log of pressure *vs.* the log of volume. The three runs gave $\frac{n}{m} = 1.7$; $\frac{n}{m} = 2.1$ and $\frac{n}{m} = 2.3$. From the constant pressure runs V^2 was proportional to Θ and, therefore, $m = 1$, and since in all sludges studied *m* has had values of 0.8 to 1.0 we took $m = 1$; therefore, *n* was equal to $\frac{n}{m}$. If *m* did equal 0.8 instead of 1.0 the value of *n* would be approximately 1.6 instead of 2. What interested us and what we were trying to show was that for constant rate runs *n* was greater than unity.

4—With respect to the fourth criticism we believe it better to plot all data and draw a representative line than to compare point with point. Graph 2 in our article shows that the points themselves vary and we took the general trend or slope of these points as our representative line.

5—Although not pointed out by Mr. Sperry, the equation which he proposes as fundamental is designed to be applicable only to runs made under constant pressure, and hence is not general. This is true because it is derived by means of an integration in which the pressure P is placed outside of the sign of integration, and the expression integrated, holding P constant. As shown by the tests described in our article, constant rate of flow filtration is fundamentally different from constant pressure and the equation derived for one is not directly applicable to the other.

Further, the real use of a law of filtration should be to afford a means of calculating sizes of filter equipment, which involves an area term. At no place in Mr. Sperry's equation does such an area term appear, nor is it readily apparent how the equation could be translated into terms of area of filtering medium.

It is acknowledged that the equation of Lewis and Almy used in calculating the results of the tests described was derived for constant pressure operation and is not strictly applicable in its present form to constant rate of flow conditions. As a result, important progress is being made in research work to alter the equation so that it will hold for both constant pressure and constant rate of flow conditions. However, the equation as it is holds rigidly for constant pressure runs at different pressures, whereas the equation proposed by Mr. Sperry does not, as can be shown by plotting the data of Lewis and Almy, and determining the constants in Mr. Sperry's equation at various pressures. These are found not to be constant at all for different pressures, when the runs are made with the same sludge under otherwise identical conditions. The equation Mr. Sperry proposes probably holds for incompressible sludges such as sand or kieselguhr, but it will not hold for gelatinous precipitates.

6—In regard to the criticism that our plant tests were made on commercial apparatus of too crude a nature for determining factors of a fundamental formula, I wish to call attention to the fact that we were not trying to determine the formula, as that had been done by Lewis' and Almy years before. We were simply applying the formula to plant-scale equipment for the purpose of testing the application of theory to practice. While we admit that Lewis' equation is not at present complete for constant rate of flow, its simplicity and also its complete applicability to constant pressure conditions made it satisfactory as a starting point for investigations in constant rate of flow filtrations.

That the mathematical treatment of filtration is still undeveloped is apparent when one tries to determine for a given sludge the best filtration method, *i. e.*, the proper thickness of cake and whether the cycle should be at constant pressure or constant rate of flow, together with the proper pressure or rate.

F. P. Baker

School of Chemical Engineering Practice
Massachusetts Institute of Technology
Cambridge, Mass.
September 6, 1921

The Variability of Crude Rubber

Editor of the Journal of Industrial and Engineering Chemistry:

In a recent paper [This Journal, 13 (1921), 519] Mr. J. B. Tuttle describes results of experiments which led him to the conclusion that a simple mixing of rubber and sulfur is not suitable for the purpose of testing the variability in rate of cure of plantation rubber, because (1) the variability shown by such a simple mixture is much greater than that met with in the factory where it is usual to add varying quantities of organic and inorganic accelerators, and (2) because one particular synthetic product is found actually to retard vulcanization except in the presence of zinc oxide, when it acts as a powerful accelerator. The author therefore concludes that all tests on crude rubber should be performed on mixtures to which have been added from 2 to 5 per cent zinc oxide.

As my name is mentioned with others as favoring the simple mixing of rubber and sulfur for testing purposes, I would take the opportunity of pointing out that I have used for some time a mixing containing zinc oxide but of late have confined myself to a simple rubber-sulfur mix for routine testing purposes as I did not find that the presence of zinc oxide had any appreciable effect on the results. Mr. Tuttle will admit that it is only a few powerful accelerators such as the CS_2 condensation product of dimethylamine and homologs, termed by Bruni "ultraaccelerators" which are much influenced by the presence of basic oxides, in particular zinc oxide, and he has not shown that accelerators of this type are present in crude rubber. Unless such are present the addition of zinc oxide is superfluous.

I am in many ways in agreement with Mr. Tuttle's general arguments, in that I consider the basis of the mixture employed for testing should be broadened so as to include ingredients commonly used in the rubber factory. It is however impossible to make up and test a large number of different mixtures for each sample of plantation rubber under examination. Under these circumstances it is wisest to employ the simplest mixture possible, namely, rubber and sulfur only. Moreover, provided a sufficiently large proportion of sulfur is used, this mixture has the advantage that it accentuates variations inherent in the raw rubber. It is consequently more sensitive than mixings containing organic and inorganic accelerators. On the other hand, the almost exclusive use of this simple mixture by chemists in the East has given rise to a false impression as to the variability of plantation rubber, as it has been assumed that variations similar to those found with this mixture would also be experienced with the technical mixtures in the factory. If Mr. Tuttle will refer to my publications he will note that I have carried out many experiments with litharge and other ingredients and have emphasized the importance of a wider basis for raw rubber testing.

HENRY P. STEVENS

15 BOROUGH HIGH ST.
LONDON BRIDGE, S. E. 1
LONDON, ENGLAND
August 4, 1921

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Editor of the Journal of Industrial and Engineering Chemistry:

Dr. Stevens states that he has tried zinc oxide and did not find it to have any appreciable effect on the results. It will be quite apparent that zinc oxide will eliminate any retarding effect caused by small amounts of acid, and hence cannot fail to have some effect in reducing that part of the variability which is due to impurities in the rubber, and not to variations in the rubber itself.

He is quite mistaken in assuming that it is only a few accelerators, such as the dimethyldithiocarbamates, which are influenced by the presence of basic oxides; some of the weaker accelerators, such as thiocarbanilide, are absolutely ineffective in the absence of basic fillers. In this country, it is an almost universal custom to have some basic oxides present in any compound containing organic accelerators, although there are some with which this is not necessary.

There can be no question regarding the impossibility of using a large number of formulas for testing rubber; one should suffice, and the simpler the formula, the better. However, we must not lose sight of the fact that we are testing the quality of the crude rubber, and not whether or not there are minute amounts of organic accelerators which have been retained during the process of coagulation, etc. Hence, we should use the simplest formula which will develop the facts regarding the crude rubber **only**. If the simple formula of rubber and sulfur would do this, there could be no objection to its use, but the facts are against it. Dr. Stevens' experiments with zinc oxide and with litharge show that he, like many others, has felt the urgent need for some better way of testing crude rubber than by the simple formula of rubber and sulfur. He admits that the almost exclusive use of this formula by the chemists in the East has given rise to a false impression as to the variability of plantation rubber. Well, if the use of this formula by the plantation laboratories produces false impressions, what else can we expect in the laboratories of the consumers? Is it not logical to suppose that they will have as large variations in their crude rubber tests as have been shown by the chemists of the Far East? And when they do obtain these differences, will they not feel a certain prejudice against plantation rubber which may be, and in my opinion is, absolutely unwarranted?

Dr. Stevens has surely compared the rate of vulcanization by means of the rubber-sulfur mixture, of an exceptionally clean, thoroughly washed rubber, with the so-called "slab rubber." The former, containing practically no impurities, will hardly vulcanize at all; the latter, with all sorts of fermentation products, vulcanizes rapidly. A vulcanization test of this type would condemn the former; in other words, we are placing a premium on fermented rubber; on delay in coagulation; on poorly washed rubber; on general carelessness and poor management. In the face of the excellent results obtained in the industry with the use of plantation rubber, we dare not accept the logical conclusion. Obviously there is an error in our argument and equally obviously, the error lies in the means by which we measure quality.

Practically every one interested in the subject believes that there is some variability in plantation rubber (confining our argument to standard high grades only, the poorer grades necessarily are not comparable). I feel, and from what he has written I believe that Dr. Stevens agrees with me, that the amount of this variability is very much less than has been popularly supposed to exist. We have been sticking to an antiquated and wholly insufficient test because of the seeming impossibility of getting a new and better one adopted. Perhaps I did not go far enough in my suggestion regarding the improvement in the testing formula; it might have been better to have included the suggestion that to the rubber, sulfur, and zinc oxide, we add sufficient organic accelerator to cure properly the standard high grades of plantation rubber. There can be no logical objection to organic accelerators; we know that some crude rubbers contain them, and they materially aid in the vulcanization, and to add such an accelerator would merely tend to a greater uniformity. Just which one should be used is a matter which could be decided by the leading plantation chemists. The consumers are in the unfortunate position that by reason of their ignorance as to the manner of preparation, they are unable to make these tests effectively—they must be made at the place where the rubber is prepared. It will be a great step forward if the planters and consumers could get together on this subject and find out the true amount of variability, its causes, and the means for its elimination.

JOHN B. TUTTLE

68 BANK ST.
NEW YORK, N. Y.
August 20, 1921

The Nitrogen Supply of the World

Editor of the Journal of Industrial and Engineering Chemistry:

The nitrogen demand and supply has of late been the subject among us of much thought and discussion. It is indeed one of the most important and far-reaching problems with which the chemist has to deal. For this reason, it has seemed to me worth while to prepare for the benefit of the readers of THIS JOURNAL a brief digest of a recently published German book[1] dealing with this subject.

The title of the book is "The Nitrogen Supply of the World;" the author, Walter Eucken. It discusses the subject solely from the point of view of economics, mentioning only incidentally the chemical, biological, and technical aspects of the subject. The periods before, during, and after the world war are treated in separate sections.

In the section devoted to the pre-war period an account is given of the development, both of the demand for and supply of nitrogen throughout the world. There is also a careful description of the world's nitrogen market as it then existed, including its organization, its method of fixing prices, and the syndicates and cartels which dominated it.

The section devoted to the war period is divided into two parts, one dealing with the situation in Germany, the other with that in allied and neutral countries. The first part is especially interesting to us. The author states that the total German nitrogen supply on hand in April 1914 plus that captured later in Antwerp, Ostende, and northern France amounted to 50,000 tons. In 1913 to 1914 the coke ovens and gas works in Germany produced 110,000 tons, but with the initial slump in the iron industry at the beginning of the war this dropped to 65,000 tons of nitrogen per year. There was a small arc installation (Pauling) at Muldenstein, near Bitterfeld, in the brown coal region designed to operate on off-peak power in peace time, and another similar plant was started at Zschornewitz in the same region in 1915. There was also an arc plant at Rhina in Baden operated by electricity supplied by Swiss water power. In 1917 the plant at Muldenstein had to shut down on account

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[1] "Die Stickstoffversorgung der Welt; Eine volkswirtschaftliche Untersuchung," by Walter Eucken. Deutsche Verlags-Anstalt, Stuttgart, 1921. 185 pp. 23.5 × 15.5 cm. Price M. 28. Bound in half linen, M. 35.

of the coal shortage, that at Rhina because of technical difficulties and that at Zschornewitz blew up—so that these installations never made any significant contribution to the nitrogen supply. There were cyanamide plants at Knapsack and Tröstberg with a combined output of 12,000 tons of nitrogen per year, while the Haber-Bosch plant at Oppau had an output of 7000 tons with a new plant under construction which assured a supply of 30,000 tons per year. Altogether, these several sources would furnish something like 110,000 tons of nitrogen per year.

This supply, together with the 50,000 tons on hand, appeared adequate for all the German military requirements. But it was immediately evident that the residue available for agriculture would be wholly inadequate, for in 1913 Germany had used 215,000 tons of nitrogen in fertilizers. Vigorous measures were therefore taken at once to increase the supply of nitrogen. Walter Oswald discovered that the addition of chlorides prevented the decomposition of ammonia at high temperatures in the retorts, and facilitated its condensation; but this advantage was minimized and attempts to increase the supply of nitrogen from this source checkmated by the stagnation in the iron industry and the resultant lessened coke production. The cyanamide plants at Knapsack and Tröstberg were enlarged to furnish 22,000 tons, new plants were erected at Waldhut in Baden to produce 8000 tons, at Pisteritz in central Germany to produce 30,000, and at Chorzow in upper Silesia to produce 15,000 tons, making a total of 75,000 tons of nitrogen per year from cyanamide. The Haber-Bosch plant at Oppau was further enlarged to yield about 70,000 tons and another similar plant was started at Merseburg to yield 30,000 tons of nitrogen per year. These sources, with the 65,000 tons from coal, would give in the early part of 1916 an output of 240,000 tons of nitrogen per year. Estimating the military requirements at 60,000 tons, the residue of 180,000 tons, if not ample, still appeared to be adequate as an emergency supply of nitrogen for agriculture.

But the calculations proved to be utterly illusory. In the first place, the rated outputs because of unavoidable technical difficulties were almost never fully attained. In the second place, the military requirements increased far beyond any expectation. The so-called "Hindenburg program" proposed on August 31, 1916, and soon adopted, required for military purposes alone 240,000 tons of nitrogen per year—or an amount equal to the total rated output!

The Germans redoubled their efforts. The by-product output, thanks to the tremendous metal requirements of the Hindenburg program, would be 100,000 tons per year. The cyanamide plants could be but slightly expanded because of the great coal requirements, but the Haber-Bosch plant at Merseburg was enlarged to yield 130,000 tons, making a total output of 390,000 tons of nitrogen per year. Actually these enormous outputs were not fully realized. The coke ovens and gas plants did indeed produce in 1917 to 1918, 100,000 tons, but the cyanamide plants produced only 66,000 and the Haber-Bosch plants 105,000 tons—or a total of 271,000 tons of nitrogen. German agriculture, which in 1914 took 215,000 tons of nitrogen in commercial fertilizers, actually received in 1915 to 1916, 79,000, in 1916 to 1917, 109,000, and in 1917 to 1918 only 92,000 tons of nitrogen. In other words, in spite of its tremendous expansion, the German fixed nitrogen industry was only able to keep pace with the military requirements, and German agriculture never got more than 40 per cent of its peace-time requirements of commercial nitrogen. Its supply of nitrogen in the form of manures showed a corresponding deficit.

The author points out that this deficiency of nitrogen was one of the most important reasons for the decrease in the productivity of German soil during the war, and was therefore one of the economic reasons for the collapse of Germany. He therefore questions whether the efforts to increase the nitrogen supply, in spite of their magnitude and their success in meeting the immediate military requirements, can be looked upon as successful.

The final section, devoted to the post-war situation and the outlook for the future, both in Germany and outside of Germany, is also of much interest. In Germany, while the population has decreased about 11 per cent during the war the total available human food supply has decreased nearly 40 per cent. This has resulted in a marked increase in mortality in urban population and a marked decrease in industrial efficiency. Importation of foodstuff offers no solution of the difficulty—for it requires an increase in the export of manufactured goods, and this is impossible until adequate nourishment is secured. The only way out is to increase the domestic production of foodstuff and the prime necessity here is an increase of nitrogenous fertilizer. If only the amount corresponding to the consumption in 1913 to 1914 were to be used, 445,000 tons of artificial nitrogen would be required because of the great diminution in the supply of manure. The actual yearly output of the partly completed war plants is put at 310,000 tons of nitrogen—so that, instead of the overproduction which was predicted during the war—there is an acute domestic demand for all the nitrogen which these plants can produce.

The production in Chile, too, in spite of the many technical and economic improvements introduced during and after the war, has shown a marked decline as compared with war and prewar figures. In the United States there has been a marked increase in the production of by-product ammonia, but this has been balanced by a corresponding decrease in the supply from similar sources in England, Belgium, and France, caused by difficulties in the coal mining industry, difficulties which are but slowly disappearing. On the other hand, the author emphasizes that there must be a marked increase in the demand for nitrogenous fertilizer all over the world as compared with pre-war times because of the greatly increased recognition of its importance. All told, therefore, he sees a world-wide demand for all the nitrogenous fertilizer which can reasonably be produced in the near future.

So far as the relative advantage of nitrogen from cyanamide *versus* that from Haber-Bosch ammonia is concerned, the author states that in spite of the relative cheapness of Haber-Bosch ammonia, because of the high cost of sulfuric acid, cyanamide nitrogen is cheaper in Germany than the nitrogen of ammonium sulfate. He also expresses his confidence that in spite of the disturbing effects of anomalous industrial conditions and depreciated exchange in Chile, German fixed nitrogen will be able to compete successfully with Chile saltpeter at least in Germany after, just as it did before the war.

Harvard University
Cambridge, Mass.
September 6, 1921

Arthur B. Lamb

Adoption by the Colleges of Standard Metric Units—Addendum

This paper by Dr. Eugene C. Bingham was presented at the "Special Order on World's Standardization" before the Division of Industrial and Engineering Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

The investigation of white clays east of the Mississippi River has been practically completed at the Ceramic Experiment Station of the U. S. Bureau of Mines, at Columbus, Ohio. The results indicate that none of the clay samples were similar to English china clay, which under the microscope is seen to be composed largely of plate-like particles, whereas the American clays, particularly secondary kaolins, contain more or less irregular or amorphous particles. The primary kaolins from North Carolina resemble English clay more closely in physical appearance than other clays, but have a much coarser grain and contain more free silica than English clay.

SCIENTIFIC SOCIETIES

Synthetic Organic Chemical Manufacturers Association of the United States

Representative manufacturers of synthetic organic chemicals met at the Hotel Washington, Washington, D. C., on October 28 and 29 to effect a comprehensive national organization of the several closely related lines of manufacture included in this branch of chemical industry.

The name of the new organization is Synthetic Organic Chemical Manufacturers Association of the United States. Its purposes, as set forth in the Constitution adopted, are

> To advance the science of organic chemistry by encouraging the manufacture in the United States of all kinds of organic chemicals; to coöperate with the various agencies of the Government of the United States in its efforts to develop, improve and render serviceable a complete organic chemical industry; to promote cordial relations between American concerns and individuals engaged in the production and use of organic chemicals; to afford means for the dissemination of scientific knowledge; to promote the highest scientific and business standards in relation to the industry; and generally to take such collective action as may be proper for the establishment and perpetuation of the organic chemical independence of the United States of America.

The Association is subdivided into four Sections—Dyestuffs, Pharmaceuticals, Intermediates, and Fine Organic Chemicals, each Section having a vice president, a secretary, and an executive committee.

The administration of the Association is in the hands of a Board of Governors, consisting of the president, the four vice presidents, and ten members nominated by the Sections.

The following officers were elected:

President: CHAS. H. HERTY, formerly editor of THIS JOURNAL.

Vice Presidents: C. N. TURNER, Dyestuff Section; HERMAN SEYDELL, Pharmaceutical Section; S. W. WILDER, Intermediate Section; B. T. BUSH, Fine Organic Chemical Section.

Messrs. R. S. Burdick, R. C. Jeffcott, August Merz, M. R. Poucher, P. Schleussner, and F. P. Summers were elected members of the Board of Governors. The remaining four members, one from each Section, will be elected later.

The president and the four vice presidents are *ex-officio* members of the Board of Governors.

After adjournment Dr. Herty gave out the following statement:

> At last there has been brought together one effective organization of men who, for the past five years, have been developing in this country all lines of manufacture of synthetic organic chemicals. The fine spirit shown throughout the meetings gave assurance of a strong organization which will aid in developing to its maximum efficiency this industry born of the war period and now recognized by all as being of such fundamental importance to the nation.
>
> Much progress has been made, but there is a long road ahead before we can hope to give to our country an industry which can worthily meet its every need. Toward that goal we are facing. The Association as organized is thoroughly democratic in character. It follows national lines in this respect, for in the councils of the Association the small manufacturer has equal voice with the larger and we all recognize that the success of the industry is closely bound up in the welfare of the small manufacturer. There have been some points of friction in the past between producer and consumer, but I believe that the hearty spirit of coöperation is developed which in the end will assure the future of this industry. Personally it seems strange to me to be leaving the ranks of the chemists for those of the manufacturers. For six years I have editorially striven to arouse first the chemist and then our people in general to the importance of developing this industry. The idea is now so clear to all that I feel my best efforts can be given to work with the manufacturers on their many problems in the hope of aiding them in the firm establishment of that industry which is so vitally important to this nation that Secretary Hoover, in his address to us last night, while emphasizing that the main consideration now was the development of this industry for utilization of waste, added: "In these days of the development of forms of warfare that we have to exist under, it is fundamental and vital to us that we should maintain those industries on which we are bound to depend for our very vital existence if we ever come to conflict."

The 1921 Meeting of the Association of Official Agricultural Chemists

About 400 members and visitors attended the annual convention of the Association of Official Agricultural Chemists, which was held at the Washington Hotel, Washington, D. C., October 24 to 26, 1921. The usual reports of referees, associate referees, and committees were presented, as well as a number of special papers. Much new work was reported and the interest manifested in all the sessions was highly gratifying.

Honorable Henry C. Wallace, Secretary of Agriculture, welcomed the visitors to Washington in behalf of his department and expressed the belief that the chemist of the future must contribute even more largely than he has in the past not only to the utilization of surplus crops but to the utilization of waste products of all kinds. Dr. Harvey W. Wiley, honorary president of the Association, postponed an operation on his eyes in order to address the Association and delivered one of his inimitable extemporaneous addresses. He stated that the outstanding feature in the realm of chemistry during the past year was the reception tendered Madame Curie on her recent visit to this country. He called special attention to the progress that has been made in the utilization of human foods for dietary purposes, referring particularly to the recent health exhibit at Cincinnati and the similar exhibit to be held in New York City in November. He indicated that one of the big problems of the agricultural chemist of the future was to produce a greater yield per acre—that there must soon be a reflection of the activities of the Association in an economic sense. He strongly urged upon the Association the importance of expressing all business relations in chemicals in metric units and the Association, in one of its later sessions, adopted the following resolution:

> *Resolved,* that this Association endorses the proposal now under consideration by Congress that after due notice the metric system of weights and measures be made the legal system of the United States and also, to further the introduction of this system, recommends that its members in the purchase of supplies, designate and describe the same in terms of the metric system so far as possible.

Dr. W. F. Hand chose for his presidential address "Tendencies of Recent Research on the Photosynthetic Processes of Plants, giving a short historical account of the discovery of fundamental facts regarding carbon assimilation and a discussion of some of the more important theories and experimental work of recent years.

The work completed this past year affords the chemist who is specially interested in the estimation of small amounts of boric acid two reliable methods which, with little further modification, should meet the requirements demanded. The method which was presented for the adaptation of Clark and Lubs' indicator and buffer solutions to the production of an exactly neutral ammonium citrate should greatly lighten the burden of the chemists making the determination of reverted phosphoric acid. Those interested in the production of precipitated phosphates for use in the fertilizer industry noted with interest the important change in the method of analysis of this class of materials authorized by the Association. Several special papers of importance in the determination of nitrogen, phosphoric acid, and small amounts of potash were received with interest.

The Committee on Vegetation Tests on the Availability of Phosphoric Acid in Basic Slag completed its investigations and the detailed report will be published later in the *Journal of the Association of Official Agricultural Chemists.* The committee declared the Wagner method to be a reliable procedure for measuring the available phosphoric acid in basic slag phosphates and recommended its adoption as the official method of the Association.

A committee of five, consisting of H. D. Haskins, J. W. Kellogg, E. G. Proulx, G. S. Fraps, and R. N. Brackett, was appointed to consider definitions of terms and interpretation of results of fertilizer analyses.

The attendance in the Drug Section was the largest in the history of the organization and the program was the most extensive that has ever been presented. Papers relating to the estimation of arsphenamine, neoarsphenamine, alkaloids, silver and silver proteinates, santal oil, acetylsalicylic acid, peppermint oil, and crude drugs were presented and, in some cases, methods of analysis for these products were adopted.

The following committee was appointed to coöperate with the Revision Committee of the United States Pharmacopeia: L. F. Kebler, H. C. Lythgoe, H. C. Fuller, A. R. Bliss, and W. S. Hubbard.

Senator E. F. Ladd, many years an active member in the Association and at one time its president, was called out of town and was unable to address the Association as planned. By unanimous vote, however, he was elected an honorary life member of the Association, as was also Dr. C. L. Alsberg, former secretary of the Association.

Dr. R. W. Balcom, chairman of the Board of Editors, presented a report of progress showing a very material increase in the number of subscribers to the *Journal* of the Association. He stated that the first edition of the "Official and Tentative Methods of Analysis" had been exhausted and that the second edition was now available for distribution. He called particular attention to the fact that the Association has practically caught up in the publication of its back proceedings and within a very few months will be in a position to print original contributions.

A resolution was adopted urging the Congress of the United States to continue adequate, beneficial legislation until the various chemical industries in this country have become firmly established. The Association further expressed its hearty endorsement of the aims and purposes of the Conference on the Limitation of Armament to be held in Washington, D. C., beginning November 11, and expressed the hope that the highest aims and purposes of the Conference on the Limitation of Armament may be attained.

The following officers were appointed for the ensuing year:

Honorary President: HARVEY W. WILEY *President:* F. P. VEITCH
Vice President: A. J. PATTEN *Secretary-Treasurer:* W. W. SKINNER

Additional members of the Executive Committee are H. D. Haskins and R. E. Doolittle.

The names of members of committees, referees, and associate referees for the year 1922 may be secured through the Secretary. The full proceedings of the convention will be printed in the *Journal of the Association of Official Agricultural Chemists.*

N. A. PARKINSON

BUREAU OF CHEMISTRY
WASHINGTON, D. C.
October 28, 1921

Calendar of Meetings

American Institute of Chemical Engineers—Annual Winter Meeting, Baltimore, Md., December 6 to 9, 1921.

American Association for the Advancement of Science—Annual Meeting, Toronto, Canada, December 27 to 31, 1921.

American Ceramic Society—21st Annual Meeting, St. Louis, Mo., February 27 to March 2, 1922.

Cornerstone Laid for New Cornell Chemical Laboratory

The cornerstone of the new $1,500,000 chemical laboratory at Cornell University was laid by the donor, George Fisher Baker, a New York financier and philanthropist, October 20, 1921. Mr. Baker is 81 years of age and has been for years one of the foremost figures in America's finance and industry and has been interested in Cornell University for a number of years, having given in the past a total of $335,000 to the University for residential purposes, in addition to the magnificent donation of the chemical laboratory.

At the exercises held first in Bailey Hall and later at the site of the new building, President Farrand, the newly elected head of the University, presided. An organ prelude by Professor Quarles was followed by the invocation given by the Rev. President Rush Rhees, D.D., LL.D., of the University of Rochester. President Farrand then introduced Professor Emeritus Edward L. Nichols, former dean of the College of Arts and Sciences at Cornell, who made a preliminary address in which he assured the donor of the new building that "if the chemists and students of chemistry who are to work in this building attain only an average output as measured by the performances of university laboratories in the past, the donor may count on returns from his investment such as no commercial enterprise has ever paid."

Dr. Edgar Fahs Smith, president of the American Chemical Society, then briefly reviewed the development and changes which have taken place in the laboratory during the last 100 years. He traced the gradual expansion of the science of chemistry and predicted a great future for it as a result of the splendid research work that is now being carried on.

The program further included an address by Mr. Charles M. Schwab of the Board of Trustees of the University and an address by Prof. L. M. Dennis, head of the department of chemistry, which included a description of the contents of the box of records to be placed in the cornerstone.

The President, the speakers, delegates from other universities and colleges, trustees and the faculty, then led the procession to the site of the new laboratory. The box of records was deposited within the cornerstone by Mr. H. A. Ley, the builder of the laboratory, after which Mr. George F. Baker, the donor, laid the cornerstone.

The contract calls for the completion of the building 100 weeks from the time the ground was broken, last July, and it is now planned to build the ground floor and the first floor, if possible, this fall.

Local Section Meetings

CHICAGO SECTION

December 16—John Johnston, "University and Industrial Research."

EASTERN NEW YORK SECTION, SCHENECTADY

December 9—E. Newton Harvey, "Animal Light."
January —Saul Dushman, "The Quantum Theory."

WESTERN NEW YORK SECTION, BUFFALO

December 20—E. F. Smith.
February 21—A. D. Little.
March 7—E. E. Slosson, "Popularization of Science."

MARYLAND SECTION

December 8—(Joint meeting with A. I. C. E. convention).
J. C. W. Frazer, "Oxidation of Carbon Monoxide to Dioxide at Room Temperatures by a Catalyst."
R. W. Wood, "Ultraviolet Light."

NEW YORK SECTION

December 9—Discussion of Editorial Policy, J. I. E. C.

Honorary Members of the American Chemical Society

At the recent meeting of the AMERICAN CHEMICAL SOCIETY Sir William J. Pope and M. Paul Kestner were elected to honorary membership in the SOCIETY. The following letters of acceptance have been received:

The Chemical Laboratory
The University, Cambridge
30 September, 1921

THE SECRETARY,
THE AMERICAN CHEMICAL SOCIETY,
WASHINGTON.

DEAR MR. SECRETARY:

In electing me one of its Honorary Members the American Chemical Society has done me a great honour and one which I very deeply appreciate.

During my seventeen years membership of the Society I have always been keenly interested in its work and have watched with admiration the rapidity with which it has become, under wise and vigorous management, the largest and one of the most useful chemical organizations in the world.

Whilst asking you to convey my thanks to the Society for the signal distinction conferred upon me may I express that hope that the American Chemical Society may continue its rapid development and become an even more efficient medium for cementing the interests of English-speaking chemists.

Believe me, Dear Mr. Secretary,
Yours very sincerely,
(*Signed*) WILLIAM J. POPE

. . . .

38 Rue Ribiera, Paris
15 October, 1921

MR. CHARLES L. PARSONS,
AMERICAN CHEMICAL SOCIETY.

DEAR MR. SECRETARY:

Your intimation that the American Chemical Society has done me the signal honour of electing me as one of its few honorary members has afforded me the very greatest pleasure and I beg of you to convey to your President and Council the expression of my very sincere thanks.

I am the more sensible of the honour done me in that I feel it to be connected with my association with the Société de Chimie Industrielle. My colleagues in our Society share with me my gratitude for the honour you have bestowed on their president.

It was a matter of keen regret to me that I was unable for a variety of reasons to come over and take part in your annual meeting last month. I had looked forward with much pleasure to making this trip and to seeing you and many of my American friends once more.

Believe me,
Yours sincerely
(*Signed*) PAUL KESTNER

An Englishman's Impressions of the New York Meeting

Because of the international scope of the New York meeting of the American Chemical Society with the Society of Chemical Industry, it is of particular interest to note the impressions of our foreign guests. The "Impressions of an English Chemist" printed in the *Chemical Age*, London, October 8, evidently reflect the thoughts of a number of the foreign visitors to the 62nd Meeting of the American Chemical Society.

The English chemist was favorably impressed with the extent of the membership of the American Chemical Society and the large percentage of this membership which attended the meeting. The splendid recognition given the proceedings of the Society in the public press likewise drew favorable comment from the English visitor. He states that because of the excellent organization of the A. C. S. News Service "the American receives doses of scientific knowledge at regular intervals; he finds it not unpleasant, reads it, and so becomes reasonably well informed on such matters." The writer further observes that the American chemist enjoys a more exalted state in the public mind of the average American and in the minds of his employers, than is the case in England. He observes that "In America, the term chemist means something and it is a name to be proud of for it ranks high in the professions; in England it might mean anything, for the general public knows no better." The writer then comments on the extent to which publicity has been developed for the American chemist and on the fact that the tendency is perhaps to make the level of chemical thought exchanged a little less profound than one expects at scientific meetings and "one could not help but feel that some of the speakers had their eye not so much upon their chemical audience as upon the outside public."

He sums up the source of influence of the American Chemical Society as lying, first, in its complete membership, second, in the high character of its officers, which include men of world-wide reputation in both academic and industrial circles, and, third, in the splendid publications of the Society.

In discussing the scientific aspects of the meeting he brings out the importance given to chemical warfare in the proceedings of the Society; the recognition of the close connection between the organic chemical industry in peace times and the manufacture of munitions and gases in time of war. He also calls attention to the deep thought that is engaging American chemists along the line of supplying substitutes for the energy now being derived from rapidly disappearing natural resources, such as petroleum, gas, coal, etc. It is a healthy sign in the opinion of the writer that Americans recognize the fact that they have exploited nature's gifts rather ruthlessly, and he feels that it should be a source of pride to Americans that the sins of the past are being confessed, and steps taken to secure better treatment for those natural resources which as yet remain untouched. The concluding paragraph of the writer's impressions or observations is of special interest:

> It is still possible to get rich quick in America, and the American is virile, active and as eager for riches as any other man. He is, however, prepared to work for them; he lives nearer to nature than we do and thinks very keenly about his great country of which he is so justly proud. This and that requires to be done, and until it is done there can be no rest, for as he so often says, "We are a young country yet."

Plant Excursions, New York Meeting

As chairman of the Excursion Committee during the recent joint meeting of the American Chemical Society and the Society of Chemical Industry, I wish on their behalf to express my appreciation to the management of the many industrial concerns who so generously extended their hospitality to members and visitors of the above Societies.

The spirit of coöperation shown by the management and operating staff of the plants visited aided in no small measure in making the meeting the success it was.

Tours of inspection were made through the following plants:

Seaboard By-Products Coke Co., Jersey City, N. J.
Joseph H. Wallace & Co., Stamford, Conn.
The Westport Mill, Westport, Conn.
National Lead Co., 135 Marshall Street, Brooklyn, N. Y.
Ward Baking Co., Pacific Street, Brooklyn, N. Y.
Corn Products Refining Co., Edgewater, N. J.
Astoria Light, Heat & Power Co., Shore Road, Astoria, L. I.
American Tobacco Co., 337 W. 27th St., New York City.
Ladew & Co., Lincoln Highway, Newark, N. J.
General Leather Co., Frelinghausen Ave., Newark, N. J.
Ziegel Eisman & Co., Newark, N. J.
National Biscuit Co., 10th Ave. & 15th St., New York City.
Liebmann's Sons, 36 Forrest St., Brooklyn, N. Y.
Tiffany & Co., New York City.
Manhattan Rubber Co., Passaic, N. J.
Toch Bros., 59—9th St., Long Island City, N. Y.
American Sugar Refining Co., Brooklyn, N. Y.
Keuffel & Esser Co., Hoboken, N. J.
Standard Oil Co., Bayonne, N. J.
Balbach Smelting & Refining Co., Newark, N. J.

J. V. N. DORR

Chemistry and Disarmament

Under this general heading three splendid contributions were made to the program of the New York Section of the American Chemical Society, the American Section of the Society of Chemical Industry and the New York Sections of the American Electrochemical Society and the Société de Chimie Industrielle at a joint meeting held in Rumford Hall, New York, November 18, 1921.

All doubt as to the effectiveness of the airplane with its weapons of explosive and poison gas bombs over the battleship was dispelled by the showing of the official U. S. Navy motion pictures of the bombing and sinking of the Ost Friesland, a former German cruiser, and the U. S. S. Alabama.

These pictures were supplemented by an address by Major H. S. Kimberly, formerly of the Chemical Warfare Service.

No one who saw these remarkable pictures can doubt that the day of the battleship is over and that, as Mr. Francis P. Garvan later stated, "the future safety of the nation depends upon the development of airplanes, and a chemical industry which in time of war can be quickly turned into a source of munitions and poison gases."

Both Mr. Garvan and Mr. H. E. Howe, who spoke on "Chemical Research and Business," pointed out the necessity for reiteration of the story of chemistry to the people of the nation, by chemists themselves.

WASHINGTON LETTER

By WATSON DAVIS, 1418 Rhode Island Ave., Washington, D. C.

THE CONFERENCE ON LIMITATION OF ARMAMENTS

Washington is now discussing the battleship-limiting bombshell with which Secretary Hughes inaugurated the Washington Conference on the Limitation of Armaments yesterday.

This plan for cutting the navies of the United States, Great Britain, and Japan, which will scrap 66 capital ships and which will save approximately $375,000,000 in construction and upkeep for the United States alone during the ten-year holiday, will result, if adopted, in bringing chemical warfare and the use of aircraft into greater prominence. This is the current opinion here.

Naval armament limitation is without a doubt the most important step planned for the conference, and the success of the other steps in the agenda is largely dependent on the fate of this first proposal. The second topic under "Limitation of Armaments" in the official agenda is "Rules for control of new agencies of warfare," and it is under this head that the discussion of chemical and aerial warfare will come. It is not expected now that the conference will begin to discuss these matters for at least a week or ten days, perhaps not before this letter appears.

The American delegation to the conference has selected an advisory and technical staff to aid them in the various problems of the conference. Herbert Hoover, Secretary of Commerce, is the only technically trained member of the advisory committee of twenty-one members, but included on the technical staff are: Dr. Edgar F. Smith, president of the American Chemical Society; General C. C. Williams, chief of Ordnance; General Amos A. Fries, chief of the Chemical Warfare Service; General George O. Squier, chief of the Signal Corps; William S. Culbertson, United States Tariff Commission; Dr. S. W. Stratton, director of the Bureau of Standards; Dr. J. H. Dellinger, chief of the radio investigations of the Bureau of Standards; L. W. Austin, radio specialist, Navy Department. It is understood that most of the advisory work in connection with chemical warfare will be in the hands of Dr. Smith, General Fries, and army and navy officers.

If the reduction in naval armament is accomplished and chemical and aerial methods come into the foreground, it is pointed out that the world will be adopting methods of warfare that are best suited for defense. Aggressive warfare between nations separated by more than 200 to 300 miles of water is difficult without battleships. Airplanes spreading gas can operate most effectively for only 100 to 200 miles from their base, but for defensive purposes this distance would be ample. From the standpoint of economy, there is hardly any comparison between the old and new forms of warfare.

The question of electrical communication will also be considered by the conference. This will include land telegraphs, cables, and radios. Of these, wireless will hold the most important place. It is entirely probable that at least a good beginning toward definite rules regulating international radio communication will be made. The work is expected to be in the nature of the continuation of that of the recent Paris conference.

EXTENSION OF EMERGENCY TARIFF LAW

Uncertainty as to the present emergency tariff law and the dye licensing provision has been cleared up by the action of the Senate Finance Committee, which has agreed to the House resolution extending this measure until February 1 or until such time as the permanent tariff schedules are enacted into law. Hearings on the agricultural schedules of the permanent tariff bill are planned during the coming week.

THE TAX BILL

The tax bill is now out of the Senate and in conference with the House Committee. The tax on nonbeverage alcohol diverted to beverage purposes, which would have been collected on all alcohol and refunded upon proof of legitimate use, has been eliminated, although high taxes for nonbeverage use are provided. The objectionable "guilty until proved innocent" provision would have tied up a large amount of capital for chemical and drug manufacturers. The tax bill as it came out of the Senate has two provisions, both of which double the tax on nonbeverage alcohol or medicinal liquors if they are illegally used. If whiskey and alcohol used in making official preparations or in chemical manufacture find their way into illegal hands, the tax may be as high as $25.60 a proof gallon.

MUSCLE SHOALS

Mr. Ford's negotiations for Muscle Shoals have reached the point where Secretary of War Weeks and Mr. Ford, with their experts, are discussing details. The Secretary of War recently made an inspection trip to the nitrate plant and power plant projects. On November 18 there will be a personal conference between Mr. Ford and Mr. Weeks. As Congress must give the War Secretary specific authority to sell or lease any public grounds, any agreement they reach must be ratified by Congress.

THE JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY

Washington chemists are looking forward to the establishment of the editorial offices of the *Journal of Industrial and Engineering Chemistry* in this city, and they will welcome in his new job as editor Mr. Harrison E. Howe, who has been here as resident chairman of the Division of Research Extension of the National Research Council.

Dr. Chas. H. Herty, who has resigned as editor to become president of the Synthetic Organic Chemical Manufacturers Association of the United States, which was organized in Washington last week, carries with him the appreciation of Washington chemists for his work in bringing the *Journal* to its present high plane, and he has their hope for as much success in his new position as with the *Journal*.

THE WASHINGTON SECTION OF THE A. C. S.

The Washington Section of the SOCIETY held its annual election of officers on November 10 with the following results: Dr. R. C. Wells, of the Geological Survey, president; J. B. Reed, Bureau of Chemistry, secretary; H. W. Houghton, Hygienic Laboratory, treasurer; Dr. W. D. Collins, Geological Survey, Dr. R. B. Sosman, Geophysical Laboratory, Dr. W. W. Skinner, Bureau of Chemistry, Dr. W. M. Clark, Hygienic Laboratory, Dr. William Blum, Bureau of Standards, retiring president, councilors; C. W. Bacon, Bureau of Plant Industry, V. K. Chesnut, Bureau of Chemistry, Dr. L. H. Adams, Geophysical Laboratory, F. C. Cook, Bureau of Chemistry, C. O. Appleman, University of Maryland, R. O. E. Davis, Bureau of Soils, members of the executive committee.

The SOCIETY portrait of Joseph Priestley, discoverer of oxygen and pioneer American chemist, was presented to the National Museum on October 25 by President Edgar F. Smith, at a meeting arranged by the local section. Dr. Charles D. Walcott, secretary of the Smithsonian Institution, accepted the portrait on behalf of the Museum. Dr. F. W. Clarke told of the formal founding of the AMERICAN CHEMICAL SOCIETY at Priestley's former home in 1876.

CORROSION OF BURIED PIPES

An extensive investigation of the corrosive action of soil on pipes used for gas and water mains and service pipes has been undertaken by the Bureau of Standards of the Department of Commerce. The Bureau has the coöperation of the Bureau of Soils, the pipe manufacturers, and the public utilities through the Research Subcommittee of the American Committee on Electrolysis.

Forty locations have been selected as representative of the principal families of soils to be found throughout the United States and at each will be buried a number of samples of every kind of iron and steel pipe in commercial use. These field tests will be supplemented by laboratory tests which will give complete data on the physical and chemical properties of the soil and on the microstructure, complete metallurgical history, and chemical analysis of the pipe specimens.

It is expected that the experiment will continue for eight or ten years.

Hearings are being held before the House Committee on Rivers and Harbors on bills to prevent pollutions of waters in rivers and harbors. Manufacturing chemists have urged that before steps were taken that would interfere with a large number of manufacturing plants the Secretary of Commerce be requested to conduct a scientific investigation into the causes of water pollution.

The Geological Survey has made public the report on the superpower system. This system would link up power plants and industrial plants 150 miles inland from Boston to Washington and form a gigantic electrical system that would bring about economies in power production and utilization. It is estimated that the superpower system would save annually 4,024,800 short tons of coal for chemical and metallurgical industries alone.

The National Research Council has issued a list of "American Research Chemicals," compiled by Dr. C. J. West.

November 13, 1921

PARIS LETTER

By CHARLES LORMAND, 4 Avenue de l'Observatoire, Paris, France

THE MEETING OF THE SOCIÉTÉ DE CHIMIE INDUSTRIELLE

Without having the same breadth as that of its American sister, the first meeting held by the Société de Chimie Industrielle has been a success, and the exposition which was held at the same time, although limited to dyes and laboratory materials, attracted a great number of exhibitors, a fact which augurs well for the future. The different sections of the meeting heard numerous interesting communications, purely technical, and the special meetings which were presided over by different ministers or under-secretaries of the State brought together a considerable audience where all the social elements were mingled to hear eminent masters open up new horizons on possibilities of the utilization of chemistry. These meetings have had a prolonged echo in the daily press.

The importance of the nitrogen problem, which was treated in all its aspects, has not escaped the attention of the French public who realize all that France owes to her agriculture and all that she ought to do to aid it.

As a matter of course, the lecture of Mr. Claude attracted very great attention. This lecture was given in the great amphitheater of the Sorbonne which holds more than 3000 persons. The amphitheater was full to bursting and 2000 people could not get in, so that Mr. Claude had to repeat this same lecture two days later.

In addition to his researches on ammonia, Mr. Claude developed his ideas on scientific research in general. He recalled the history of certain recent discoveries such as that of invar, that of radium, that of ammonia synthesis, the direct result of Gibbs and LeChatelier, and with these as examples, he showed the infinite variety of resources of scientific research. He insisted especially on the necessity of very attentive observation of all phenomena. In science, he said, there are no phenomena, however small they may be, which can be neglected. How many scientists have passed by great discoveries by not having pushed to their furthest limit the results of a very slight phenomenon. Is it necessary to recall that a French physicist spent several years of his life in establishing the fact that the nitrogen of the air had a density different from that of nitrogen made from ammonium nitrate? Not having carried through to the end the conclusions from this observation he missed the discovery of argon, which Ramsay isolated and characterized only a short time afterward.

Along another line, new and bold ideas of the trend of organic chemistry were developed at the meeting, and I would lay special emphasis on the last point which was treated in a masterly fashion by Sir William Pope, great chemist as well as great traveler, since we received him in Paris at the moment when he returned from attending your meeting in New York, and he has now left us to go toward the Indies.

Sir William Pope showed us that chemistry involving high potential energy has had its day. If all the efforts which have been made to accomplish the synthesis of indigo or that of camphor by purely chemical means had been directed toward the improvement of the culture of the indigo plant or the camphor tree, the yields would have been greater and, moreover, the energy in the coal or the petroleum would have been conserved. The mineral fuels existing on the globe are becoming exhausted slowly but surely. Solar energy, on the other hand, seems to be always available. Therefore, it is toward photosynthesis, in its most general sense, or rather toward the study of the intimate mechanism of the chemical phenomena of life, that we must turn our efforts. There will always be growing in the ground plants which can furnish us with oil. This oil will be a fuel which will renew itself each year, while the oil which we draw from the earth becomes exhausted, and what is true in this case can be applied to many other absolutely necessary products. This program which Sir William Pope outlines for us is evidently only a rough sketch, but each of us can draw the conclusions from it.

Another revelation of the meeting was the important place occupied by motion picture films. The committee in charge of the meeting were inspired with what had been done in the United States and tried to bring together some educational films. Unfortunately the films which were requested from the Bureau of Mines in Washington could not be sent to France where they would certainly have been as successful as the French films which were used.

Beside the films which permitted the audience to see the latest industrial processes for the manufacture of glass, cement, potassium, paper, etc., and the presentation of films which were accompanied by technical papers, a communication was devoted to the use of the motion picture as tool in the hands of the commercial traveler. A small machine, the size of a suitcase, will permit projecting on a 25 × 25 screen a film showing the operation of a machine or a piece of apparatus. The representative or the salesman can thus visit his patrons and demonstrate very easily the utilization of what he has to sell.

PROFESSOR MOUREU A DELEGATE TO WASHINGTON

In one of my preceding letters I expressed the idea that chemists ought to share in the conference at Washington. The French government, after some hesitation, has adopted this view and by the time these lines appear, Professor Moureu, member of the Institute and professor of the Collège de France, where he succeeded our great Berthelot, will be among you. The welcome which you accorded to Madame Curie makes us sure of the warmth of Mr. Moureu's reception.

The work of Professor Moureu on acetylene compounds and on the rare gases is universally known. At a time when the atomic theory was not yet adopted by all chemists, he was one of the defendants of the new faith and one of his first works was his book on "Notions fondamentales de chimie organique" from which all French chemists have learned organic chemistry. This book is already in its seventh edition in France. It has been translated in all the Latin countries; an English edition, prefaced by Sir William Pope, has just appeared. It is certainly one of the most justly celebrated of the numerous books by Mr. Moureu. I may add that during the war Mr. Moureu was president of the committee of French scientists which directed our Chemical Warfare Service. The services which he rendered in this capacity made him the natural choice for the great mission which is entrusted to him.

A NEW PETROLEUM WELL

At different times I have called your attention to researches on petroleum which are made at different places in France. A boring in the region of Bugey (department of Ain) has just given a considerable flow, which has lasted for several days. The volume of hydrocarbon gas in twenty-four hours is 100,000 cubic meters.

November 1, 1921

INDUSTRIAL NOTES

The waterworks, at Hopewell, Virginia, which during the war supplied the munitions plant of E. I. duPont de Nemours & Co., as well as adjacent villages, has been sold to the Industrial Service Corporation of Virginia which took over operation of the plant on November 1. The transfer includes electric and steam pumping stations, filtration plant, boiler plant, transmission lines, etc., the plant having a capacity of approximately 30,000,000 gal. per day.

The Universidad Nacional, Tacuba, Mexico, is installing modern equipment to be used in connection with studies in the technology and manufacture of glass.

With the completion of the dyeing plant at Greenville, S. C., a branch of the Franklin Process Co., of Providence, R. I., Greenville will have the last phase necessary to make complete a cycle in cotton manufacturing from raw to finished state. A new process will be employed in that the yarn will be dyed in the wound form instead of the skein, which has been found to be cheaper and more thorough. This will be the only plant of its kind in the South.

The Director of Sales, War Department, has announced that army surplus material costing the United States Government $209,620,147 has been transferred to other governmental departments and establishments. The Department of Agriculture received $138,290,529 worth of the material, nearly 66 per cent, and all but $10,619 of its share was transferred without funds. Acids, chemicals, etc., constituted $19,156,517 worth of the material transferred.

Representative pottery interests at Trenton, N. J., and vicinity are formulating plans to bring about an early readjustment and lowering of freight rates on commodities entering into the manufacture of sanitary pottery, including clay, feldspar, flint, etc. A committee has been appointed to compile data and carry out the details of the movement, under the chairmanship of M. D. Warren, traffic manager of the Chamber of Commerce of Trenton.

Canadian Dyes, Ltd., of Trenton, Ontario, on September 19, 1921, turned out the first batch of dyes ever manufactured in Canada, when about 1700 lbs. of Canadian Direct Blue 2B were successfully finished in the first process of making.

Standardization of the different kinds, qualities, and sizes of window and plate glass was discussed at a recent conference between glass distributors, architects, and engineers of the Bureau of Standards. The conference outlined a program that will be participated in by the manufacturers, distributors, architects, and the Bureau of Standards, and which it is believed will result in the elimination of unnecessary sizes, standardize quality, and enable a more efficient use of this material. Nomenclature in the glass industry will be studied and an effort will be made to define trade terms that are likely to be used with various meanings.

Arrangements are being made for the sale of approximately 81,000 tons of sodium nitrate from the army reserve supply, which has been recommended by officials of the Ordnance Department. The nitrate has been declared surplus and its sale is considered in the interests of the Government as it is at present stored at considerable expense in privately owned warehouses and the army is not in a position to move the 81,000 tons from the private storage into its own storehouse in which the bulk of the nitrate reserve of 300,000 tons is kept. It is expected that the Director of Sales will soon issue a statement calling for sealed proposals on all or any part, which will probably be sold f. o. b. cars.

The Synthetic Ammonia and Nitrates Co., Ltd., a new organization formed under the auspices of Brunner, Mond & Co. Ltd., of England, has commenced the laying out of new works near Middlesbrough. The plant when completed will be used for the manufacture of ammonia, nitrates, and various chemicals.

The Raymond Bros. Impact Pulverizer Company has located its permanent eastern office at 50 Church St., New York City, in charge of Mr. S. B. Kanowitz.

PERSONAL NOTES

Mr. A. P. Gloeckler has resigned as chief chemist of the Tropical Paint and Oil Co., Cleveland, Ohio, and has accepted the position of superintendent of the paint department of the Acorn Refining Co., Cleveland, Ohio.

Mr. Philip L. Gile, formerly connected with the American Agricultural Chemical Co., in their agricultural service bureau, and for eleven years prior to that position chemist of the Porto Rico Agricultural Experiment Station, is at present in charge of the division of soil chemical investigations of the Bureau of Soils, U. S. Department of Agriculture, Washington, D. C.

Mr. Alfred S. Halland has resigned as chief chemist of the National Aniline & Chemical Co., Buffalo, N. Y.

Dr. R. L. Sebastian, who was formerly connected with the Department of Health, State of Pennsylvania, in connection with work on mine drainage investigations, has joined the chemical staff of Edgewood Arsenal, Edgewood, Md.

Mr. Herbert Brunt has left the firm of Brunt Dye & Chemical Co., Manchester, England, owned by his father, and has taken over an analytical practice, established in 1870, in London. The name of the firm has been, and will continue to be, Halse and Marshall.

Mr. Thomas J. Keenan recently announced his resignation as Secretary-Treasurer of the Technical Association of the Pulp and Paper Industry in order to accept the position of editor of *Paper*, in the reorganization of which he becomes an officer and stockholder.

Mr. Noah D. Lambert, formerly assistant superintendent of the N. Y. Mutual Gas Light Co., has resigned his position and is now chief engineer and secretary of the Lambert Meter Company, Inc., of Brooklyn, N. Y.

Prof. Sidney S. Negus has recently resigned as head of the chemistry department of the Mercersburg Academy, Mercersburg, Pa., to take up graduate work for his doctorate at the Johns Hopkins University.

Mr. Edward A. Dieterle, assistant chief chemist of the Koppers Co., Mellon Institute, Pittsburgh, Pa., has been made chief chemist of the Chicago By-Product Coke Co., Chicago, Ill.

Mr. Arthur Gallun, of Milwaukee, Wis., and a member of the SOCIETY for a number of years, recently died after an attack of pneumonia. Mr. Gallun was one of the most active organizers of the Leather Division of the A. C. S., and had financed the leather chemistry research at Columbia.

Dr. Clifford S. Leonard, for the past year fellow in chemistry to Sweden on the American-Scandinavian Foundation, has completed his research at the Karoline and Nobel Institutes of Stockholm and has accepted the position of research instructor of pharmacology at the University of Wisconsin.

Mr. H. S. McAree, formerly with the Atlas Powder Co., Landing, N. J., is now engaged in the real estate and insurance business as a member of the firm of Campbell-McAree & Co., Scranton, Pa.

Mr. Leslie R. Olsen, for two years chemist and supervisor of baking operations for the Seattle Baking Co., of Seattle, Washington, has become chief chemist in charge of the laboratories of the International Milling Co., New Prague, Minn.

Mr. L. I. Shaw, assistant chief chemist and assistant chief of the Division of Mineral Technology of the Bureau of Mines, at Washington, D. C., was recently transferred to the Ceramic Station of the Bureau of Mines at Columbus, Ohio, where he is assistant superintendent and in charge of the physico-chemical work.

Mr. A. D. Camp who was formerly with the American Eveready Works, Long Island City, N. Y., has joined the Williamsport Building Products Co., Williamsport, Pa., as factory manager and development chemist.

Mr. Robert Calvert, who was director of the du Pont Company's research laboratory at Arlington, N. J., is now teaching chemistry in the University of Southern California, Los Angeles, Cal., and is also carrying on a general consulting practice.

Mr. Robert G. Dort has severed his connection with the Bregeat Corporation of America, where he was assistant to the vice president, and has become a vice president of the Allied Explorations, Inc., New York City.

GOVERNMENT PUBLICATIONS

By Nellie A. Parkinson, Bureau of Chemistry, Washington, D. C.

PUBLIC HEALTH SERVICE

Keeping Qualities of Neoarsphenamine in Ampule. G. B. Roth. Public Health Reports, 36 (October 14, 1921), 2523–39. Tables are given to show that market samples of neoarsphenamine may deteriorate in ampule under ordinary conditions. They may change in color, solubility, toxicity, mobility in ampule, and odor after varying periods. The conclusion is reached that commercial neoarsphenamine is a relatively unstable substance in ampule. The results of the experiments suggest (1) that in order to secure further data on its keeping properties, the date of manufacture might be given on the label of all lots issued; (2) that neoarsphenamine should be kept at ice-box temperature.

Comparative Toxicity of Thymol and Carvacrol (Isothymol). A. E. Livingston. Reprint 666 from Public Health Reports. 8 pp. Paper, 5 cents. 1921.

Portable Cyanide Gas Generator for Fumigating Small Compartments. C. M. Fauntleroy. Reprint 673 from Public Health Reports. 8 pp. Paper, 5 cents. 1921.

Direct Inoculation Test for B. Botulinus Toxin, Determination of Presence of B. Botulinus Toxin by Intraperitoneal Inoculation of Laboratory Animals with Suspected Foods. I. A. Bengston. Reprint 677 from Public Health Reports. 8 pp. Paper, 5 cents. 1921.

Death Erroneously Attributed to Chlorinated Water. The Pennsylvania Department of Health, on Post Mortem, Finds That Chlorinated Water Was Not the Cause of Death. From a Report by C. A. Emerson, Jr., Chief Engineer, Pennsylvania Department of Health. Public Health Reports, 36 (October 28, 1921), 2678–9. The conclusion is reached that there is not the slightest evidence that the disinfection of the public water supply had anything to do with the death in question and there is no reason to fear that the chemical disinfection of public water supplies is other than an important safeguard and protection to public health.

Digest of Comments on Pharmacopeia of United States of America. 9th Decennial Revision, National Formulary, 4th Edition, Calendar Year 1918. A. G. DuMez. Bulletin 127. 356 pp. Paper, 25 cents. 1921.

U. S. GEOLOGICAL SURVEY

Lead in 1919. General Report. C. E. Siebenthal and A. Stoll. Separate from Mineral Resources of the United States, 1919, Part I. 18 pp. Published October 6, 1921.

The following tabular statement gives the general items regarding domestic production and consumption of refined lead in short tons, for 1918–19.

	1918	1919
PRODUCTION		
Domestic desilverized lead	282, 024	208, 751
Domestic soft lead	210, 463	147, 744
Domestic desilverized soft lead	47, 418	67, 938
TOTAL	539, 905	424, 433
Foreign desilverized lead	100, 290	57, 787
Total primary[1] lead	640, 195	482, 220
Antimonial lead	18, 570	13, 874
Secondary[1] lead	97, 100	122, 100
CONSUMPTION		
Apparent consumption of primary lead, stocks disregarded	542, 975	434, 143

[1] "Primary lead," which is produced directly from ore, is here distinguished from "secondary lead," which is obtained by refining skimmings, drosses, and old metals. The statistics of secondary lead are given on p. 320. Wherever in this report the word "lead" is used without qualification it means primary lead.

Potash in 1920. M. R. Nourse. Separate from Mineral Resources of the United States, 1920, Part II. 25 pp. Published October 4, 1921.

At the beginning of 1920 the fear of large imports of foreign potash salts still harassed the domestic potash industry, still most of the 66 plants reporting production remained in operation through the year. A few plants reported operation for only the first three months of the year.

About 225,000 short tons of potash (K_2O) were imported in 1920. This, with the 48,077 short tons of domestic output, made the available quantity about equal to that normally used in each of the five years immediately preceding the world war. Because of the low prices received for their produce many of the farmers of the country were unable to take up the promissory notes given by them for fertilizer in the spring of 1920 and were also unable to buy the fertilizer they required in the fall. This condition, coupled with the abundance of potash on the market, resulted in a cancellation by the fertilizer manufacturing companies of orders for domestic potash and greatly reduced the prices of all potash fertilizer materials. As a consequence, all the Nebraska plants were closed by the end of December.

Gold, Silver, Copper, and Lead in South Dakota and Wyoming in 1919. Mines Report. C. W. Henderson. Separate from Mineral Resources of the United States, 1919, Part I. 6 pp. Published October 5, 1921. The total value of the gold, silver, and lead produced at mines in South Dakota in 1919 showed a decrease of 26 per cent as compared with the value of metals produced in 1918. The output of gold represented more than 97 per cent of the total value. There were only four producing deep mines in Wyoming in 1919, a decrease of eight mines as compared with 1918.

Antimony in 1920. F. C. Schrader. Separate from Mineral Resources of the United States, 1920, Part I. 12 pp. Published October 27, 1921. The United States in 1915–1918 produced 10,750 short tons of antimony ore, containing 4,310 tons of metal. There has been no production of ore since 1918.

DEPARTMENT OF AGRICULTURE

Composition of Cottonseed. C. F. Creswell and G. L. Bidwell. Department Bulletin 948. 221 pp. Paper, 25 cents. Published September 10, 1921. This bulletin is issued for the guidance of producers, dealers, and crushers in order that they may know more nearly the content of the product in which they are dealing and be better able to judge the value and consequently the price that can be paid for seed. It sets forth data showing as nearly as possible approximate oil and meal yields in each county of the cotton belt.

Drug Plants under Cultivation. W. W. Stockberger. Farmers' Bulletin 666. (Reprint.) 50 pp. Paper, 10 cents.

Pine-Oil and Pine-Distillate Product Emulsions: Method of Production, Chemical Properties, and Disinfectant Action. L. P. Shippen and E. L. Griffin. Department Bulletin 989. 16 pp. Issued October 7, 1921.

Standard and Tentative Methods of Sampling and Testing Highway Materials. Recommended by the Second Conference of State Highway Testing Engineers and Chemists, Washington, D. C., February 23 to 27, 1920. Department Bulletin 949. 98 pp. Paper, 25 cents. Issued October 10, 1921.

The Composition of California Lemons. E. M. Chace, C. P. Wilson, and C. G. Church. Department Bulletin No. 993. 18 pp. Paper, 5 cents. Issued October 15, 1921. A few well-defined differences between the varieties of lemons examined exist, the most striking of which is in the specific gravity of the fruit. The Villa Francas have more oil than the Eurekas. Otherwise no absolute difference in the oil content is shown. A marked difference in sugar content between Eureka and Lisbon lemons exists. There is no difference in the acid content of the three varieties. No correlation is shown between color and thickness of the peel.

Phosphorus in Fertilizer. W. H. Waggaman. Separate 840 from the Yearbook of the Department of Agriculture, 1920. 7 pp. Paper, 5 cents.

Articles from Journal of Agricultural Research

Effect of Ammonium Sulfate upon Plants in Nutrient Solutions Supplied with Ferric Phosphate and Ferrous Sulfate as Sources of Iron. L. H. Jones and J. W. Shive. 21 (August 15, 1921), 701–28.

Bacteriological and Chemical Studies of Different Kinds of Silage. C. A. Hunter. 21 (August 15, 1921), 767–89.

Sandy Crystals in Ice Cream: Their Separation and Identification. H. P. Zoller and O. E. Williams. 21 (August 15, 1921), 791–6.

Reliability of the Nail Test for Predicting the Chemical Composition of Green Sweetcorn. C. O. Appleman. 21 (September 1, 1921), 817–20.

Occurrence of Quercetin in Emerson's Brown-Husked Type of Maize. C. E. SANDO AND H. H. BARTLETT. 22 (October 1, 1921), 1–4.

Microscopic Study of Bacteria in Cheese. G. J. HUCKER. 22 (October 8, 1921), 93–100.

Further Studies on Relation of Sulfates to Plant Growth and Composition. H. G. MILLER. 22 (October 8, 1921), 101–10.

Hydrocyanic Acid in Sudan Grass. C. O. Swanson. 22 (October 15, 1921), 125–38.

Absorption of Copper from the Soil by Potato Plants. F. C. COOK. 22 (October 29, 1921), 281–7.

COMMERCE REPORTS

The Brazilian market for **chemicals, iron and steel, and electrical goods** shows improvement. (P. 261)

A distinctly optimistic feeling has arisen in the Chilean situation, due to the belief that the visit of a representative of the nitrogen pool to America will improve the **nitrate** situation. The belief is also growing that competition in artificial fertilizers has been overestimated. The economic condition appears to be better although increased consumption of nitrates by Europe and the United States must precede a definite trade revival. (P. 261)

Attention is directed to recent British developments in **stainless iron** and it is pointed out that this substance is of equal importance with stainless steel. (P. 264)

A report on the Northern Argentine **petroleum fields** is given. Figures are included showing the results of chemical analyses of oils from different localities and a complete record of the test is on file in the Bureau of Foreign and Domestic Commerce. (Pp. 276–8)

According to a decree of the Ministry of Industry and Commerce of Poland dark **crude oil** and similar products may not be exported from Poland without a license. (P. 303)

The production of **petroleum** at the Comodoro Rivadavia fields, from the wells operated by the Argentine government, was 1,936,588 bbls. during the fiscal year, and the production of other wells during the same period is estimated at 230,000 bbls., making a total of 2,266,588 bbls. (P. 314)

Copies of the Bolivian **mineral oil** concession law of June 16, 1921, are now available and may be obtained from the Bureau of Foreign and Domestic Commerce or its district and coöperative offices. (P. 315)

It is reported that the Anglo-Persian Oil Co., under the auspices of the Australian Commonwealth government, is about to prospect for **oil** in Papua, New Guinea. (P. 317)

A report on "**Alcohol Motor Spirit** and Possibilities of Its Production in British Guiana" may be consulted in the Bureau of Foreign and Domestic Commerce or at its district offices. (P. 337)

The Imperial Mineral Resources Bureau has submitted a valuable report on **fluorspar** (fluorite). (P. 341)

The production of **cellulose** in Finland is reviewed. At the end of last July the production of cellulose in Finland was being carried on with practically full force, all of the twenty-four cellulose-producing mills in the country running full time with an approximate yearly output of 300,000 tons of sulfate and sulfite. It is estimated that the total production for the year 1921 will amount to approximately 250,000 tons. (P. 345)

The **drug and chemical market** of Argentina is reviewed, and the opinion is expressed that under the present prices of these products from the United States the American manufacturer will possibly lose the market within a short time, the average difference in price between American and European drugs ranging from 40 to 60 per cent. The United States holds a strong position in the industrial trade in Argentina and with favorable prices there should be no difficulty in holding a large share of this trade. (Pp. 352–3)

The production of German **potash salts** has risen very rapidly from less than 8,000,000 tons in 1919 to over 11,000,000 tons in 1920, as is evidenced by the following tabular statement. (P. 353)

1911	9,706,507	1916	8,642,887
1912	11,070,014	1917	8,938,738
1913	11,607,511	1918	9,438,251
1914	8,171,512	1919	7,772,036
1915	6,879,476	1920	11,386,439

The British trade in **linseed** is reviewed. (P. 366)

The Imperial Mineral Resources Bureau has recently issued in its series of monographs, a report respecting **tungsten ores** and concentrates. A tabulated statement is given showing the world's production of tungsten ores from 1913 to 1919. It is pointed out that wolfram concentrates are sold on the basis of 65 per cent tungstic oxide in the British Empire and 60 per cent in the United States. (Pp. 394–5)

Quotations are given from a recent issue of the Japanese-American Commercial Weekly in which the **oil policy** to be adopted by Japan is briefly outlined. Among other things it was proposed to establish a bureau to carry out investigations. (P. 407)

The construction of **fuel-oil stations** in the Azores is reported. (P. 408)

The United Kingdom has ordered that a customs duty of $33^1/_3$ per cent ad valorem shall be paid on the following imported goods: laboratory porcelain, compounds (not including ores or minerals) of thorium, cerium, and the other rare earth metals; synthetic organic chemicals (other than synthetic organic dyestuffs, colors, and coloring matters imported for use as such and organic intermediate products imported for their manufacture), analytical reagents, all other fine chemicals (except sulfate of quinine of vegetable origin) and chemicals manufactured by fermentation process. (P. 418)

Czechoslovakia has suspended the import duties on **zinc ash, zinc slag, and dross.** (P. 418)

Italy has authorized the free admission of **colored paper pulp.** (P. 418)

Portugal has abolished export surtaxes on **carbon sulfide.** (P. 418)

Kaolin is now subject to a Portuguese surtax, but all minerals except tin and tin ore may now be exported without payment of an export surtax. (P. 419)

A reduction has been made in Rumanian export duties on **light benzene, heavy benzene, lamp oil, light oils and heavy oils.** (P. 419)

The French export prohibition on **illuminating oils** has been removed. (P. 419)

The **dyestuffs** sent to Japan as war compensation from Germany will again be sold in public tender, the first tender being deemed too low by the government. It is generally believed, however, that the second tender will only bring forth still lower offers as the dye market is daily becoming worse. (P. 425)

The production of **iron ore** in France during the first six months of 1921 was 7,532,868 tons—1,693,464 tons more than the output in the first half of 1920. (P. 453)

The **petroleum** industry in Mexico is reviewed in considerable detail. In 1913 Mexico furnished but one-fifteenth of the world's supply of oil; in 1920 it furnished nearly one-fourth. A comparison of the following figures of oil produced in Mexico, in the United States and in the world since 1901, indicates the phenomenal growth of this industry in Mexico. (Pp. 463–8)

Years	Mexico Bbls.	United States Bbls.	Total World Production Bbls.
1901	10,345	69,620,529	167,434,434
1902	40,200	88,766,916	182,006,076
1903	75,375	100,461,337	194,879,669
1904	125,625	117,080,960	218,204,391
1905	251,250	134,717,580	215,292,167
1906	502,500	126,493,936	213,415,360
1907	1,005,000	166,095,335	264,245,419
1908	3,932,900	178,527,355	285,552,746
1909	2,713,500	183,170,874	298,616,405
1910	3,634,080	209,557,248	327,937,629
1911	12,552,798	220,449,391	344,174,355
1912	16,558,215	222,935,044	352,446,598
1913	25,696,291	248,446,230	383,547,399
1914	26,235,403	265,762,535	403,745,342
1915	32,910,508	281,104,104	427,740,129
1916	40,545,712	300,767,158	461,493,226
1917	55,292,770	335,315,601	506,702,902
1918	63,828,326	355,927,716	514,729,354
1919	87,072,955	377,719,000	544,885,000
1920	163,540,000	443,402,000	688,474,251[1]
1921 (first 6 months)	98,827,665	236,675,000[1]	....

[1] Estimated.

A final and interesting report has been issued by the Department of Scientific and Industrial Research in regard to **nitrogen** products in which it is observed that no definite conclusions are yet possible as to the post-war demand for fixed nitrogen, and especially that required for fertilizing purposes. (P. 469)

The resin, turpentine, pitch, and **naval stores** industry in Spain is controlled by La Union Resinera Espanola, which has recently made an alliance with the German firm for the purpose of enlarging its activities. The new company will engage in the manufacture of products derived from the distillation and refining of resin, and fish and olive oils. It will make varnishes, enamels, prepared driers, paints, linoleum, glue, aniline and other chemicals, including synthetic camphor. (P. 470)

Statistics are given showing the production and sales of **resinous products** in Spain for the years 1915–19. (P. 470)

The production of resin and similar products in Portugal for the years 1916–1921 is shown. (P. 471)

On the Tyne the Walbottle Coal and Fireclay Co., Ltd. has decided to change from the production of coal to the making of coal by-products. (P. 472)

A recent French decree increases the import tariff by fixing coefficients on the following articles: liquid chlorine, ordinary hydrochloric acid, liquid sulfurous acid, sulfate of aluminium, alum of ammonium and of potassium, peroxide of barium, and chloride of magnesium. (P. 477)

The restriction of the exportation of bauxite, together with the 20 per cent ad valorem duty, has been removed. (P. 478)

An Italian decree extends until December 31, 1921, the period during which saccharin, and the raw materials from which it is made, may be placed on sale in Italy. (P. 479)

The mineral resources of the Balkan and Near Eastern Countries are described, particular attention being directed to the minerals of Anatolia and the production of petroleum in Egypt. (Pp. 488–9)

The petroleum industry in Mexico is reviewed in an article which deals with the laws affecting the development of Mexican oil fields, court decisions, and regulations governing oil exploitation in Mexico. (Pp. 515–9)

The situation of the oil companies in Rumania is more satisfactory at present than it has been since the war. (P. 519)

Negotiations concerning the Polish oil resources are to be renewed. (P. 519)

A very promising but undeveloped oil field is thought to exist in the extreme north of Siam. Seepages have been found and it is understood that some shallow borings have yielded petroleum of a good quality with an asphalt base. (P. 519)

The British supply of antimony is described. (Pp. 526–7)

A new German process has been devised to utilize rice waste. The process is reported to be a simple chemical reaction whereby cellulose, coke filter material and paraffin, phenolin, carbonic-acid gas, carbon monoxide, hydrogen, and acetic acid are obtained in sufficient quantities to be of commercial use. (P. 550)

STATISTICS OF EXPORTS TO THE UNITED STATES

EUROPE—(P. 263)
Pig iron
Tin plate

GREECE—(P. 306)
Tanning extracts
Tanning materials
Olive oil, edible
Olive oil for mechanical uses

BELGIUM—(P. 524)
Varnish, nonalcoholic
Paints and dyes except logwood

PALESTINE AND SYRIA—(P. 306)
Olive oil, edible

NORWAY—(P. 345)
Wood pulp, chemical
Wood pulp, mechanical

LONDON, ENGLAND—(P. 365)
Tin
Drugs and chemicals
Leather
Hides
Gums

SOUTH AFRICA—(P. 378)
Concentrates:
  Lead and copper
  Vanadium
Copper, excluding matte
Copper matte
Copra
Corundum, crystalline
Hides, cattle:
  Dry
  Wet, salt
Ore:
  Copper
  Chrome
  Corundum, excluding crystals
  Corundum, crystals
  Manganese
  Vanadium
Wax

SWITZERLAND —(P. 498)
Aniline dyes

BOOK REVIEWS

Estate Rubber—Its Preparation, Properties, and Testing. By O. DE VRIES. xi + 649 pp. Drukeryen Ruygrok & Co., Batavia, 1920. Price, 20 fl. (about $6.50).

It is extremely difficult to outline adequately, within the limits of a review, the contents of the above volume. The book is not, as it makes no pretense to be, a treatise on our present scientific knowledge regarding the preparation and properties of raw rubber, but it is rather a vade-mecum for the up-to-date rubber estate manager or chemist, from which both are left to draw their own conclusions. The book is written largely from the results of researches carried out by the author or under his direction at the Institute, Buitenzorg, Java. Contemporary literature has been carefully cited and extracted, and but for the fact that much of the earlier scientific literature is unmentioned, the volume might be considered as a most valuable work for reference purposes.

In the opening chapters the composition and properties of the latex are described in great detail, and the influence of coagulants, anticoagulants, antiseptics and other chemicals, and methods of treatment of the latex on the composition and properties of the raw rubber and serum are discussed. One chapter is devoted entirely to a comparison of smoked sheet rubber with first latex crepe, based on physical and chemical tests made by the author and others. That the actual difference between these two well-known grades of commercial rubber is as insignificant as the author would have us believe will be hard to convince American rubber manufacturers. There are chapters on the keeping qualities of rubber, forms of deterioration and defects in raw rubber, and on special methods of preparation of rubber, including a comparison of the Brazilian method.

The succeeding chapters deal with the vulcanization of raw rubber and with the methods employed by the Institute of Buitenzorg for the evaluation of samples of rubber, raw or vulcanized. The reason for leaving the treatment of this subject for the latter part of the book is not obvious, particularly as methods of testing are referred to, time and again, in the earlier chapters. A complete and detailed account of the method of mixing, vulcanizing and physical testing employed by the Institute and used in connection with the preparation of the curves and data sheets employed in the book, is given. In our opinion the physical tests are insufficient really to differentiate the inner properties of different rubbers from a manufacturing standpoint, or to bring out the extent of these differences.

The final chapter is devoted to the chemical composition of raw rubber and to the judging of raw rubber on the exterior. The book is so replete with data and curves bearing on the various factors influencing the preparation and properties of raw rubber that it should be read with interest by estate managers and rubber chemists alike. D. SPENCE

Technical Records of Explosives Supply, 1915-1918. I. Denitration of Spent Acids. 56 pp., 25 illustrations. 12s. 6d. **II. Manufacture of Trinitrotoluene (TNT).** 116 pp., 63 illustrations. 17s. 6d. Ministry of Munitions and Department of Scientific and Industrial Research, London, H. M. Stationery Office, 1920. 19 x 28 cm. each.

These are the first two of a special series of reports designed to make results of technical and scientific value gained in the development and operation of the National Factories during the war available to the industries concerned. As all the factories of the country were under governmental supervision and control there was an unparalleled opportunity to secure accurate data on a large scale which was insured by the plan of chemical control instituted by Mr. Kenneth B. Quinan, and these publications represent an endeavor to retrieve some of the enormous wastage of war.

The titles of these books well indicate the nature of their contents, but though, in Volume I, it is pointed out that guncotton spent acids are denitrated in "stills," and those from TNT and nitroglycerin by steam in columns or "denitrators," only the latter method is dealt with in detail, emphasis being laid particularly on TNT acids. Likewise, regarding the nitration of toluene, while the several step by step and the single stage processes are each considered, for purposes of detailed description the plant at Queen's Ferry is taken, as it was the largest, erected on a very extensive scale, and embodied the results of a very wide engineering knowledge of chemical plants. At Oldbury a continuous process plant was erected with a rated capacity of 100 tons per week which proved capable of producing some 500 tons per week, starting with MNT from Borneo spirit.

The figures consist largely of folded plates (some 110 by 52 cm. in area) giving plans, to scale, of the apparatus, or of diagrams, such as that of the "ultimate destination of nitrogen in TNT manufacture," which enable one to apply the most precise checks at all points. In addition there are diagrammatic schemes of operation which state the masses, temperatures, and times involved with such definiteness it would be difficult to fail in manufacture if they were followed. Moreover copies of blank forms such as "TNT Washers—Sulfite Purification" for factory use add to the assurance of success.

This series of reports is prepared by Mr. W. Macnab and they are presented in excellent form for use, being printed in fourteen point, clear faced type, on heavy calendered paper, while the text is remarkably free from typographical errors, and the dimensions make the books quite convenient for use. The only suggestion to be made which would render the valuable contents of these admirable volumes more easily accessible is the addition of indexes, and a more liberal use of titles on the plates.

Everyone engaged in the production of sulfuric, nitric, and mixed acids, in the recovery of spent acids, or in conducting nitration processes, will need these books, while no student of chemical engineering should be permitted to graduate until he has become acquainted with their contents and worked out problems based on the information they convey.

Charles E. Munroe

A French-English Dictionary for Chemists. By Austin M. Patterson. xvii + 384 pp. John Wiley & Sons, Inc., New York, 1921. Price, $3.00, postpaid (18s. net).

The importance of French chemical industry was brought home to most American chemists by the magnificent effort made by French chemists during the war. We are all familiar, of course, with the achievements of the French scientific chemistry as differentiated from the applied side of our science, but the increasing importance of the latter has made it necessary for technical chemists to consult French publications more and more, and the need of a compact dictionary giving particular attention to technical meanings and interpretations has been increasingly felt. That need is admirably provided for in the volume under consideration.

"A really good dictionary is a growth," truly says the author in the preface, and naturally one cannot expect a first edition to be free from imperfections. There are several matters that will need attention in a subsequent edition.

The geographical nomenclature leaves much to be desired. There are some very important omissions and many inconsistencies. Peru, Bolivia, and Brazil are given, but neither Chile nor the Argentine Republic. The spelling in English and French is very similar in all of these and if one is given the others should be given also. A more serious omission occurs in the translation of the French word *argentin*, which is given only as "silvery," whereas it means also pertaining to or coming from the Argentine Republic. The French Departments and cities should receive more extended attention. Auvergne is not mentioned at all and the adjective *auvergnat*, meaning coming from Auvergne, is translated only in its technical meaning of "tanning liquor." This might prove to be puzzling to those unfamiliar with French geography. Of our own states California is given but not Louisiana, although the difference in the French and English spelling is the same in both cases. Havre and Havana are never spoken of singly in French but always accompanied by the article, *Le Havre, La Havane*, just as we always say "The Hague" and not merely "Hague." Many other additions of geographical names and especially adjectives would be valuable.

The objection might be made that the above suggestions might interfere with the compactness of the Dictionary, but in many other respects it could be cut down so as to make more than the necessary room for the geographical terms that are likely to be met in technical literature. Is it necessary to translate under *alcool* a long list of rather rare alcohols, such as myricyl alcohol, octyl alcohol, piperonyl alcohol, etc.? No serious hardship would entail to the chemical profession by having those of its members who work with these compounds look up the meaning of *caprylique, myricique, piperonilique* under the letters "C,""M," and "P" instead of having them thus doubly classified. Under *bleu* there is also a long list such as Berlin blue, Nicholson's blue, Prussian blue, etc., which could be safely omitted. Lives there a chemist with soul so dead that on finding that the French word *acide* means "acid" he must needs have a special reference to tell him that *acide-H* means H-acid and *acide-G* means G-acid?

The French evolved during the war an extensive nomenclature, supposedly a secret code, for the designation of war gases. The secrecy, however, proved to be more apparent than real, as captured documents proved later and although the names were mostly abandoned towards the end of the war, they are to be found in much of the French literature on war gases (*Chimie et Industrie*, **2**, 1377). It might be helpful to the future chemists engaged in research in chemical warfare to have some of the more common ones included in the dictionary. "Yperite" was the only one noticed.

The feminine gender has been the cause of several slips which should be corrected in the next edition. The adjectives of *Burette anglais, Boisson fermenté, Chaine anglais, Eau sedatif, Eau thermal, Etoupille fulminant, Etuve esterilizateur, Herbe empoisonné, Huile lithargé, Huile lythargyré, Masse demi-affiné, Poudre brisant* should be changed to the feminine. Those of *Flacon marine, Procedé marseillaise, Carton minerale* should be changed to the masculine. *Atelier de teinture* should be changed to *Atelier de peinture* if it is to mean a painter's studio. *Acier nickelé* should be translated as "nickel plated steel" as well as "nickel steel" as both meanings are common, especially the former, which was omitted. *Artifice d'éclairant* should be *artifice éclairant* as *éclairant* is an adjective and not a noun. *Avocatier* is not an alligator pear but the tree bearing alligator pears. *Blanc de Holland* should be *Blanc de Hollande.*

In the chemical nomenclature there are a few omissions. Butalanine is given, but neither butane nor hexane. *Etain gris* is translated as "bismuth," an antiquated appellation going back to the alchemists, whereas the more important translation of "gray tin" is omitted. These, however, are few and not very important.

Some translations might be objected to. *Arme blanche* is translated as "side arm." This is not correct. It means a cutting, or piercing, steel weapon. A revolver is a side arm but not an *arme blanche*, and a spear is an *arme blanche* but not a side arm.

The English proofreading has been excellent, only one misprint coming to the reviewer's attention: namely, "nickel plating" on page 240 which is misspelled "nickle plating."

But after all, these are only minor criticisms. The author has done an excellent piece of work in bringing together in a very compact form a vast number of technical words and phrases, the meanings of which would be difficult to find even in the largest dictionaries, except at the cost of much labor. With the increasing importance of French technical publications this dictionary should be found in every chemical library, public or private, in the university as well as in the technical laboratory.

The printing, paper, and the flexible binding are of the best and the book is highly recommendable as a useful purchase.

J. Enrique Zanetti

NEW PUBLICATIONS

Aluminium and Its Alloys. C. Grard. 184 pp. Constable & Co., Ltd., London.

Animal Proteins. Hugh Garner Bennett. (Industrial Chemistry Series.) 287 pp. Price, $3.75. D. Van Nostrand Co., New York.

Benzine and Mineral Lubricants, Their Production, Testing and Uses. Translated from the German of J. Formanek. Revised. 256 pp. Illustrated. Price, 15s. net. Scott, Greenwood & Son, London.

Bleaching: Being a Resumé of the Important Researches on the Industry Published during the Years 1908-1920. S. H. Higgins. (Economic Series.) 137 pp. Price, $3.75. Longmans, Green & Co., New York.

Chemical Disinfection and Sterilization. S. Rideal and E. K. Rideal. 313 pp. Price, 21s. Arnold & Co., London.

Chemical Warfare: Riddle of the Rhine: Chemical Strategy in Peace and War. V. Lefebure. 277 pp. Price, 10s. 6d. W. Collins Sons & Co., Ltd., London.

Colloids: The Chemistry of Colloids. W. W. Taylor. 532 pp. Price, 10s. 6d. net. Edward Arnold, London.

Combustibles et Huiles de Graissage pour Moteurs Diesel. W. Schenker. 94 pp. Price, 13fr. Dunod, Paris.

Combustibles Industriels. F. Colomer and Charles Lordier. 4th Edition. 704 pp. Price, 60fr. Dunod, Paris.

Cosmetics. Theodor Koller. 3d Edition. 269 pp. Price, $3.50. D. Van Nostrand Co., New York.

Dictionary: Popular Chemical Dictionary. C. T. Kingzett. 375 pp. Price, $4.00. D. Van Nostrand Co., New York.

Famous Chemists: The Men and Their Work. Sir William Tilden. 296 pp. Price, 12s. 6d. G. Routledge & Sons, London. E. P. Dutton & Co., New York.

Fixation of Atmospheric Nitrogen. John Knox. 121 pp. Price, 4s. net. Gurney & Jackson, London.

Food Chemistry: Méthodes Actuelles d'Expertises Employées au Laboratoire Municipal de Paris et Documents sur les Matières Relatives a l'Alimentation. André Kling. 326 pp. Illustrated. Price, 32fr. net. Dunod, Paris.

Food Products, Source, Chemistry and Use. E. H. S. Bailey. 2d Edition, revised. 550 pp. Price, $3.00. P. Blakiston's Son & Co., Philadelphia.

Handbook of Chemistry and Physics. Charles D. Hodgman, M. F. Coolbaugh and C. E. Senseman. 8th Edition. 711 pp. Price, 24s. Chapman & Hall, Ltd., London.

Industrial Hydrogen. Hugh S. Taylor. A. C. S. Monographs. 200 pp. Price, $3.50. Chemical Catalog Co., Inc., New York.

Inorganic Chemistry: Notes on Inorganic Chemistry. F. Francis. 244 pp. Price, 8s. 6d. net. Simpkin, Marshall, Hamilton, Kent & Co., Ltd., London.

Laboratories: Their Plannings and Fittings. A. E. Munby. 220 pp. Price, 25s. net. G. Bell & Sons, Ltd., London.

Leather Chemistry: Practical Leather Chemistry. Arthur Harvey. 193 pp. Price, $3.75. Crosby, Lockwood & Son, London.

Metallurgy: Traité de Métallurgie Générale. Léon Guillet. 541 pp. Illustrated. Price, 50fr. J.-B. Baillière, Paris.

Microscopy: Critical Microscopy. Alfred C. Coles. 104 pp. Price, 7s. 6d. net. J. & A. Churchill, London.

Modern Chemistry, Pure and Applied. Arthur J. Hale. Vol. I. 272 pp. Vol. II. 276 pp. Price, 16s. net per volume. Virtue & Co., London.

Oil-Field Practice. Dorsey Hager. 310 pp. Illustrated. Price, $3.00. McGraw-Hill Book Co., Inc., New York.

Organic Chemistry: An Introduction to Organic Chemistry. D. L. Hammick. 258 pp. Price, 6s. net. G. Bell & Sons, Ltd., London.

Organic Chemistry: Study Questions in Elementary Organic Chemistry. Alexander Lowy and Thomas B. Downey. 91 pp. Price, $1.00. D. Van Nostrand Co., New York.

Organic Syntheses. Roger Adams, Editor-in-Chief. 84 pp. Illustrated. Price, $1.50. John Wiley & Sons, Inc., New York.

Qualitative Analysis: A Textbook of Qualitative Analysis of Inorganic Substances. Sydney Alexander Key. 80 pp. Price, 7s. 6d. net. Gurney & Jackson, London.

Silver Ores. H. B. Cronshaw. 152 pp. Price, 6s. net. John Murray, London.

Soil Conditions and Plant Growth. E. J. Russell. (The Rothamsted Monographs on Agricultural Science.) 406 pp. Price, $5.00 net. Longmans, Green & Co., New York.

Tanning Materials. Arthur Harvey. 174 pp. Crosby, Lockwood & Son, London.

Waste in Industry. Committee on Elimination of Waste in Industry of the Federated American Engineering Societies. 402 pp. Price $4.00. McGraw-Hill Book Co., Inc., New York.

RECENT JOURNAL ARTICLES

Alcohol: La Fabbricazione Industriale dell' Alcool dalle Carrube. Giuseppe Mezzadroli. *Giornale di Chimica Industriale ed Applicata*, Vol. 3 (1921), No. 9, pp. 399–403.

Bearing Metals and Their Industrial Value. Z. Czochralski. *Brass World*, Vol. 17 (1921), No. 9, pp. 245–48. Abstracted from *Zeitschrift für Metallkunde*, 12, 371–403.

Blast Furnace Flue Dust—100% Recovery. George B. Cramp. *The Blast Furnace and Steel Plant*, Vol. 9 (1921), No. 11, pp. 648–53.

Cellulose: La Fabrication de la Cellulose a l'Aide du Chlore. Umberto Pomilio. *Chimie et Industrie*, Vol. 6 (1921), No. 3, pp. 267–75.

Coal: A Resumé of Standard Methods in Sampling, Analysis and Classification of Coal. A. Trevor Williams. *Journal of the Chemical, Metallurgical and Mining Society of South Africa*, Vol. 22 (1921), No. 1, pp. 1–15.

Coal: The Froth Flotation of Coal. Frank Butler Jones. *The Coal Industry*, Vol. 4 (1921), No. 10, pp. 505–09.

Dyes: Fastness of Dyeings to Storing. Oscar R. Flynn. *Textile World*, Vol. 60 (1921), No. 18, pp. 63–4.

Dyes: The Modern Dyestuff Industry. H. E. Fierz. *Journal of the Society of Chemical Industry*, Vol. 40 (1921), No. 19, pp. 364r–66r.

Electroanalyse Rapide. Arnold Lassieur. *Bulletin de la Société Chimique de France*, Vol. 19 (1921), No. 9, pp. 753–80.

Enamels: The Causes and Control of Fish Scaling of Enamels for Sheet Iron and Steel. R. R. Danielson and W. H. Souder. *Journal of the American Ceramic Society*, Vol. 4 (1921), No. 8, pp. 620–54.

Glass: The Manufacture of Glass Milk Bottles. A. L. Brown. *The Glass Industry*, Vol. 2 (1921), No. 11, pp. 259–62.

Glass: The Manufacture of Glass with Indigenous Alkali. J. P. Srivastava and D. Sinha. *Journal of Indian Industries and Labour*, Vol. 1 (1921), Part 3, pp. 333–40.

Hydrogen Ion: The Colorimetric Method of Determining Hydrogen-Ion Concentration: Some Applications in the Analytical Laboratory. Norman Evers. *The Analyst*, Vol. 46 (1921), No. 547, pp. 393–99.

Leather: Notes on Water Extraction of Leather. F. P. Veitch and R. W. Frey. *Journal of the American Leather Chemists' Association*, Vol. 16 (1921), No. 9, pp. 491–502.

Leather: The Effect of Atmospheric Humidity on the Determination of Moisture in Leather. F. P. Veitch and T. D. Jarrell. *Journal of the American Leather Chemists' Association*, Vol. 16 (1921), No. 10, pp. 547–58.

Leather: The Removal of Elastin during Bating. Robert H. Marriott. *Journal of the Society of Leather Trades' Chemists*, Vol. 5 (1921), No. 8, pp. 280–88.

Leather: Some Applications of Synthetic Tanning Materials. J. B. Hill and G. W. Merryman. *Journal of the American Leather Chemists' Association*, Vol. 16 (1921), No. 9, pp. 484–91.

Leather: Swelling of Hide Powder. Part I. Eric C. Porter. *Journal of the Society of Leather Trades' Chemists*, Vol. 5 (1921), No. 8, pp. 259–67.

Paper: Fundamental Chemistry in Paper Making. J. L. A. Macdonald. *Paper*, Vol. 29 (1921), No. 7, pp. 12–17; *Pulp and Paper Magazine of Canada*, Vol. 19 (1921), No. 42, pp. 1067–69.

Paper: Die Verwendung von Warme und Kraft in der Papierindustrie. Fredrik Grewin. *Der Papier-Fabrikant*, Vol. 19 (1921), No. 38, pp. 1025–32.

Rubber: The Acceleration of Vulcanization by Organic Accelerators. A. Maximoff. *The Rubber Age*, Vol. 10 (1921), No. 1, pp. 11–12, 14; *Le Caoutchouc et la Gutta Percha*, 1921, 10944–47.

Salvarsan: Le 606 ou Salvarsan. M. Toussaint. *Chimie et Industrie*, Vol. 6 (1921), No. 3, pp. 296–304.

Steel: Carbonizing in Fused Sodium Carbonate. Walter A. Jayme. *Forging and Heat Treating*, Vol. 7 (1921), No. 10, pp. 507–12.

Steel: Forging Experiments with Mild Steels. Paul Junkers. *Forging and Heat Treating*, Vol. 7 (1921), No. 10, pp. 518–24. Translated from *Stahl und Eisen*, 41, 677–78.

Steel: Low Temperature Carbonization and Its Relation to the Iron and Steel Industry. A. Thau. *The Blast Furnace and Steel Plant*, Vol. 9 (1921), No. 11, pp. 645–48.

Sugar: Use of Invertase for Sucrose Estimation. T. Swann Harding. *Sugar*, Vol. 23 (1921), No. 10, pp. 546–48.

Vulcanization Tests on Hexamethylene Tetramine, Formaldehyde Aniline and Aldehyde Ammonia. C. S. Williams. *The India Rubber World*, Vol. 65 (1921), No. 2, pp. 101–06.

Zirconia Cements. Mark Sheppard. *Journal of the American Ceramic Society*, Vol. 4 (1921), No. 8, pp. 662–68.

MARKET REPORT—NOVEMBER, 1921

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

INORGANIC CHEMICALS

		Nov. 1	Nov. 15
Acid, Boric, cryst., bbls	lb.	.12¾	.12¾
Hydrochloric, com'l, 20°	lb.	.01½	.01½
Hydriodic	oz.	.19	.19
Nitric, 42°	lb.	.07	.07
Phosphoric, 50% tech	lb.	.12	.12
Sulfuric, C. P.	lb.	.07	.07
Chamber, 66°	ton	17.00	17.00
Oleum 20%	ton	22.00	22.00
Alum, ammonia, lump	lb.	*.03½	*.03¾
Aluminium Sulfate (iron-free)	lb.	.03	.03
Ammonium Carbonate, pwd	lb.	*.07	*.07
Ammonium Chloride, gran	lb.	*.07	*.07
Ammonia Water, carboys, 26°	lb.	.08	.08
Arsenic, white	lb.	.06	.06
Barium Chloride	ton	*60.00	*60.00
Nitrate	lb.	*.07¾	*.07
Barytes, white	ton	28.00	28.00
Bleaching Powd., 35%, works	100 lbs.	2.25	2.25
Borax, cryst., bbls	lb.	.05¾	.05¾
Bromine, pure	lb.	.20	.20
Calcium Chloride, fused	ton	28.75	28.75
Chalk, precipitated, light	lb.	.03½	.03½
China Clay, imported	ton	18.00	18.00
Copper Sulfate	100 lbs.	5.25	5.25
Feldspar	ton	8.00	8.00
Fuller's Earth	100 lbs.	1.00	1.00
Iodine, resublimed	lb.	3.50	3.50
Lead Acetate, white crystals	lb.	.12	.12
Nitrate	lb.	.15	.15
Red American	100 lbs.	.08	.08
White American	100 lbs.	.06½	.06½
Lime Acetate	100 lbs.	2.00	2.00
Lithium Carbonate	lb.	*1.40	*1.40
Magnesium Carbonate, tech	lb.	.10	.10
Magnesite	ton	72.00	72.00
Mercury flask	75 lbs.	*38.00	*40.00
Phosphorus, yellow	lb.	.30	.30
Plaster of Paris	100 lbs.	1.50	1.50
Potassium Bichromate	lb.	.11	.11
Bromide, imported	lb.	*.14	*.15
Carbonate, calc., 80–85%	lb.	.05	.05
Chlorate, cryst	lb.	*.06½	*.06½
Hydroxide, 88–92%	lb.	*.05½	*.05½
Iodide, bulk	lb.	2.60	2.60
Nitrate	lb.	.08	.08
Permanganate, U. S. P.	lb.	*.18	*.16
Salt Cake, bulk	ton	17.00	17.00
Silver Nitrate	oz.	.48	.45½
Soapstone, in bags	ton	12.00	12.00
Soda Ash, 58%, bags	100 lbs.	2.15	2.15
Caustic, 76%	100 lbs.	4.00	4.00
Sodium Acetate	lb.	.04	.04
Bicarbonate	100 lbs.	2.25	2.25
Bichromate	lb.	.08	.08
Chlorate	lb.	.07½	.07½
Cyanide	lb.	*.27	*.27
Fluoride, technical	lb.	*.10	*.10
Hyposulfite, bbls	100 lbs.	3.50	3.50
Nitrate, 95%	100 lbs.	2.45	2.45
Silicate, 40°	lb.	.01½	.01½
Sulfide 60% fused	lb.	.06	.06
Bisulfite, powdered	lb.	.04½	.04½
Strontium Nitrate	lb.	*.12	*.12
Sulfur, flowers	100 lbs.	3.00	3.00
Crude	long ton	20.00	20.00
Talc, American, white	ton	18.00	18.00
Tin Bichloride	lb.	.18	.18
Oxide	lb.	.40	.40
Zinc Chloride, U. S. P.	lb.	.35	.35
Oxide, bbls	lb.	.09	.09

ORGANIC CHEMICALS

		Nov. 1	Nov. 15
Acetanilide	lb.	*.29	*.29
Acid, Acetic, 28 p. c.	100 lbs.	2.50	2.50
Glacial	lb.	.10	.10
Acetylsalicylic	lb.	.56	.65
Benzoic, U. S. P., ex-toluene	lb.	.65	.65
Carbolic, cryst., U. S. P., drs.	lb.	.09	.10
50- to 110-lb. tins	lb.	.21	.21
Citric, crystals, bbls	lb.	*.45	*.45
Acid (*Concluded*)			
Oxalic, cryst., bbls	lb.	.15	.14
Pyrogallic, resublimed	lb.	1.75	1.75
Salicylic, bulk, U. S. P.	lb.	.20	.22
Tartaric, crystals, U. S. P.	lb.	*.28	*.28
Trichloroacetic, U. S. P.	lb.	4.40	4.40
Acetone, drums	lb.	.12½	.12½
Alcohol, denatured, complete	gal.	.40	.40
Ethyl, 190 proof	gal.	4.75	4.75
Amyl Acetate	gal.	2.15	2.15
Camphor, Jap, refined	lb.	.74	.91
Carbon Bisulfide	lb.	.06½	.06½
Tetrachloride	lb.	.10½	.10½
Chloroform, U. S. P.	lb.	*.38	*.38
Creosote, U. S. P.	lb.	.40	.40
Cresol, U. S. P.	lb.	.17	.17
Dextrin, corn	100 lbs.	2.45	2.45
Imported Potato	lb.	.08½	.08½
Ether, U. S. P., conc., 100 lbs.	lb.	.16	.14
Formaldehyde	lb.	*.11	*.10½
Glycerol, dynamite, drums	lb.	.12½	.12½
Methanol, pure, bbls	gal.	.85	.85
Pyridine	gal.	1.75	1.75
Starch, corn	100 lbs.	1.88	1.88
Potato, Jap	lb.	.06	.06
Rice	lb.	.18	.18
Sago	lb.	.04	.04

OILS, WAXES, ETC.

		Nov. 1	Nov. 15
Beeswax, pure, white	lb.	.37	.37
Black Mineral Oil, 29 gravity	gal.	.22	.22
Castor Oil, No. 3	lb.	.10½	.10½
Ceresin, yellow	lb.	.08	.08
Corn Oil, crude, tanks, mills	lb.	.07¾	.07¾
Cottonseed Oil, crude, f. o. b. mill	lb.	.07	.06¾
Linseed Oil, raw (car lots)	gal.	.67	.69
Menhaden Oil, crude (southern)	gal.	.33	.33
Neat's-foot Oil, 20°	gal.	1.00	1.00
Paraffin, 128–130 m. p., ref	lb.	.06	.06
Paraffin Oil, high viscosity	gal.	.45	.45
Rosin, "F" Grade, 280 lbs.	bbl.	*6.00	6.00
Rosin Oil, first run	gal.	.35	.35
Shellac, T. N.	lb.	.65	.64
Spermaceti, cake	lb.	.30	.30
Sperm Oil, bleached winter, 38°	gal.	1.73	1.73
Stearic Acid, double-pressed	lb.	.10	.10
Tallow Oil, acidless	gal.	.75	.75
Tar Oil, distilled	gal.	.60	.60
Turpentine, spirits of	gal.	.83	.80

METALS

		Nov. 1	Nov. 15
Aluminium, No. 1, ingots	lb.	.17	.17
Antimony, ordinary	100 lbs.	4.85	4.85
Bismuth	lb.	1.55	1.65
Copper, electrolytic	lb.	.13	.13
Lake	lb.	.13	.13
Lead, N. Y.	lb.	.04¾	.04¾
Nickel, electrolytic	lb.	.41	.41
Platinum, refined, soft	oz.	78.00	78.00
Quicksilver, flask	75 lbs. ea.	*38.00	*40.00
Silver, foreign	oz.	.70	.70¾
Tin	lb.	.28	.28
Tungsten Wolframite	per unit	3.25	3.25
Zinc, N. Y.	100 lbs.	5.00	5.00

FERTILIZER MATERIALS

		Nov. 1	Nov. 15
Ammonium Sulfate, export	100 lbs.	2.65	2.65
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		4.50	4.50
Fish Scrap, domestic, dried, f. o. b. works	unit	3.50 & .10	3.50 & .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	.75	.75
Pyrites, furnace size, imported	unit	.14	.14
Tankage, high-grade, f. o. b. Chicago	unit	3.00 & .10	3.00 & .10

*Resale or Imported (not an American maker's price).

COAL-TAR CHEMICALS

		Nov. 1	Nov. 15
Crudes			
Anthracene, 80–85%	lb.	.75	.75
Benzene, pure	gal.	.27	.27
Cresol, U. S. P.	lb.	.17	.17
Cresylic Acid, 97–99%	gal.	.80	.80
Naphthalene, flake	lb.	.07	.07
Phenol, drums	lb.	.09	.10
Toluene, pure	gal.	.28	.28
Xylene, 2 deg. dist. range	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.	2.25	2.25
H	lb.	1.10	1.10
Metanilic	lb.	1.60	1.60
Monosulfonic F	lb.	2.40	2.40
Naphthionic, crude	lb.	.70	.70
Nevile & Winther's	lb.	1.40	1.40
Phthalic	lb.	.40	.40
Picric	lb.	.30	.30
Sulfanilic	lb.	.27	.27
Tobias'	lb.	2.00	2.00
Aminoazobenzene	lb.	1.15	1.15
Aniline Oil	lb.	.18	.18
Aniline Salt	lb.	.26	.26
Anthraquinone	lb.	1.50	1.50
Bayer's Salt	lb.	1.00	1.00
Benzaldehyde, tech	lb.	.45	.45
U. S. P.	lb.	1.40	1.40
Benzidine (Base)	lb.	1.00	1.00
Benzidine Sulfate	lb.	.75	.75
Diaminophenol	lb.	5.50	5.50
Dianisidine	lb.	4.75	4.75
p-Dichlorobenzene	lb.	.15	.15
Diethylaniline	lb.	1.40	1.40
Dimethylaniline	lb.	.45	.45
Dinitrobenzene	lb.	.21	.21
Dinitrotoluene	lb.	.25	.25
Diphenylamine	lb.	.65	.65
G Salt	lb.	.70	.70
Hydroquinol	lb.	1.15	90
Metol (Rhodol)	lb.	3.00	3.00
Monochlorobenzene	lb.	.12	.12
Monoethylaniline	lb.	2.00	2.00
a-Naphthylamine	lb.	.32	.32
b-Naphthylamine (Sublimed)	lb.	2.25	2.25
b-Naphthol, dist	lb.	.32	.32
m-Nitroaniline	lb.	.85	.85
p-Nitroaniline	lb.	.77	.77
Nitrobenzene, crude	lb.	.10	.10
Rectified (Oil Mirbane)	lb.	.13	.13
p-Nitrophenol	lb.	.75	.75
p-Nitrosodimethylaniline	lb.	2.90	2.90
o-Nitrotoluene	lb.	.15	.15
p-Nitrotoluene	lb.	.85	.85
m-Phenylenediamine	lb.	1.15	1.15
p-Phenylenediamine	lb.	1.70	1.70
Phthalic Anhydride	lb.	.40	.40
Primuline (Base)	lb.	3.00	3.00
R Salt	lb.	.60	.60
Resorcinol, tech	lb.	1.50	1.50
U. S. P.	lb.	2.00	2.00
Schaeffer Salt	lb.	.70	.70
Sodium Naphthionate	lb.	.70	.70
Thiocarbanilide	lb.	.40	.40
Tolidine (Base)	lb.	1.40	1.40
Toluidine, mixed	lb.	.45	.45
o-Toluidine	lb.	.25	.25
p-Toluidine	lb.	1.25	1.25
m-Toluylenediamine	lb.	1.15	1.15
Xylidine, crude	lb.	.45	.45

COAL-TAR COLORS

		Nov. 1	Nov. 15
Acid Colors			
Black	lb.	.80	.80
Blue	lb.	1.50	1.50
Acid Colors (*Concluded*)			
Fuchsin	lb.	2.00	2.00
Orange III	lb.	.50	.50
Red	lb.	1.00	1.00
Violet 10B	lb.	6.50	6.50
Alkali Blue, domestic	lb.	6.00	6.00
Imported	lb.	8.00	8.00
Azo Carmine	lb.	4.00	4.00
Azo Yellow	lb.	2.00	2.00
Erythrosin	lb.	7.50	7.50
Indigotin, conc	lb.	2.50	2.50
Paste	lb.	1.50	1.50
Naphthol Green	lb.	1.60	1.60
Ponceau	lb.	1.00	1.00
Scarlet 2R	lb.	.70	.70
Direct Colors			
Black	lb.	.70	.70
Blue 2B	lb.	.60	.60
Brown R	lb.	.85	.85
Fast Red	lb.	2.35	2.35
Yellow	lb.	1.50	1.50
Violet, conc	lb.	1.10	1.10
Chrysophenine, domestic	lb.	2.00	2.00
Congo Red, 4B Type	lb.	.90	.90
Primuline, domestic	lb.	3.00	3.00
Oil Colors			
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			
Black	lb.	.20	.20
Blue, domestic	lb.	.70	.70
Brown	lb.	.35	.35
Green	lb.	1.00	1.00
Yellow	lb.	.90	.90
Chrome Colors			
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.	.75	.75
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			
Auramine, O, domestic	lb.	2.25	2.25
Auramine, OO	lb.	4.15	4.15
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.	3.50	3.50
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.	2.00	2.00
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.	7.00	7.00
Rhodamine B, extra conc	lb.	10.00	10.00
Victoria Blue, base, domestic	lb.	5.40	5.40
Victoria Green	lb.	2.50	2.50
Victoria Red	lb.	7.00	7.00
Victoria Yellow	lb.	7.00	7.00