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EDITORIALS

Chemistry Catalyzes Commerce

IN THE present Chemical Exposition the AMERICAN CHEMICAL SOCIETY has chosen to emphasize how one single series of chemical phenomena—catalysis—plays a vitally important part in industry. That "Catalysis Revolutionizes Industry," one of the phrases on the booth sign, is indicated by the display embracing contact sulfuric acid, hydrogenated oil, the synthesis and oxidation of ammonia, the production of acetic acid from acetylene, and synthetic methanol. These and many other accomplishments may all be accredited to catalysis, which has become a new factor in international as well as national commerce. It has upset world markets. It has become a great force in the conservation of natural resources. It has enabled synthetic products to replace those found in nature. It has had a vital bearing upon food problems and has assumed an importance in peace as well as war.

But chemistry itself is a catalyst and the other phrase on the booth sign, "Chemistry Catalyzes Commerce," is justified by the accomplishments of our science on every hand. In more than one case it has been the vitalizing force in an industry. It has made many and has saved others. Its proper use has made the difference between profit and loss. It has given an advantage to more than one manufacturer, only to be lost if not properly supported and continued. The scientific spirit, through the laboratory, has brought a new outlook to many a manufacturer and has changed the tiresome routine of a business into a sort of entrancing game in which day by day new facts of interest are brought to light. Its presence has attracted a better class of people to the staff of an organization and as the value of applied science has become established the necessity of fundamental research has become clear. With it all has come a confidence which has enabled those whose business is founded upon true scientific principles to look fearlessly into the future.

Catalysis, which is but one of the many significant chemical phenomena, has already revolutionized industry. The opportunity for chemistry, the catalyst, seems unlimited in commerce.

Do You Want the Index?

DO YOU want the Second Decennial Index to *Chemical Abstracts?* If not for your immediate use, do you want it to be printed and thus made available? If so, you must send your name, address, and remittance of fifteen dollars as a first payment to the secretary of the SOCIETY before December 1, 1925. At the Baltimore meeting the Council, after reviewing all the data, voted that if the Second Decennial Index is to be compiled and published it must be financed by those who want it, since the undertaking is one of such magnitude that the SOCIETY cannot assume unaided the additional financial responsibility. The publication can be undertaken only if $90,000 is assured, which means three thousand subscriptions or their equivalent, one-half being paid in advance to make available funds necessary for the compilation of the index, the preparation of copy, and the setting of type.

To date less than one thousand members have subscribed. We know that many who insist upon having this index have overlooked the one thing necessary for them to do at the moment to assure it. Unless sufficient funds are in hand by December 1 to justify the directors in proceeding, the money received will be returned and the project abandoned. Of course, this is unthinkable in a society united upon the value of *Chemical Abstracts*. Failure to publish the index will indicate an incapacity for world leadership in chemistry and a disregard for our obligations to maintain at a high standard a publication which has become a reference work around the globe.

Do you want this index? If so, ACT!

Revival of Synthetic Rubber

IS THERE not a new opportunity for synthetic rubber made possible by the market conditions of today and those expected for the next several years?

Few raw materials used in quantity in America show wider fluctuations in price during the last dozen years or so than crude rubber. Not only have private ventures in rubber planting been wrecked by unexpected low prices, but work upon synthetic rubber, begun when promise of large return was alluring, has been more or less laid aside because of low price levels. Few realize how delicately balanced the rubber market is, and the price seems to depend more upon the stocks in hand than upon the production in the Far East. Delay in receiving a single shipment of crude rubber may cause a sharp advance in price.

With the coming of low prices, the planting of rubber trees was either wholly discontinued or carried forward on a reduced scale. Those familiar with the situation predict that by 1930 there will be a shortage of a million acres, which should have been planted at a time to increase world production to meet the anticipated demand of that year. The resumption of planting, which has accompanied higher price levels, can be expected to have no material influence until 1933 or 1934, when the new trees come into full bearing. This does not take into account the possible exhaustion of some of the older plantations in the near future. It seems reasonable to believe, therefore, that for the next ten years at least crude rubber will bring a comparatively high price, perhaps high enough again to invite the synthesis of this important complex colloid.

Although the restrictive plan for rubber export, which originated when British growers met large losses during the world-wide business slump of 1920, has had much to do with present high prices, it is not wholly to blame. The quantity production of motor cars brought a demand for tires and tubes estimated at one hundred million for 1925, requiring 350,000 tons of rubber. Then along came the balloon tires, which require more rubber per car. The public found them easy riding and the American demand for rubber forthwith jumped some 30 per cent. Notwithstanding this increase in consumption, the releases that come about by the normal action of the British Restriction Act have not been sufficient to meet the increasing consumption, stocks seem to be still depleting, and the price, which had been as low as 17$^1/_2$ cents in 1924, recently rose to $1.21 per pound and as we go to press is about 95 cents.

We remember the display of tires brought after several thousand miles of service to the Great Hall at the College of the City of New York on the occasion of the Eighth International Congress of Applied Chemistry. In his address as the official representative of Germany, Carl Duisberg stated that for some time he had used automobile tires made of synthetic rubber, and then said: "The difficulties which have been overcome were great indeed and those which still remain to be surmounted in order to produce a substance equal to Para caoutchouc in quality and capable of competing with cheap plantation rubber costing only two marks per kilo are still greater. But such difficulties do not intimidate the chemist and manufacturer; on the contrary they spur them on to further efforts. The stone is rolling and we will see to it that it reaches its destination."

Great progress has been made in synthetic organic chemistry since that time. Much more is known of colloids, of the use of high pressures and temperatures, of the functions of catalysts, and of the part played by mere traces of elements and compounds in chemical manufacturing. It would seem that the perfection of synthetic rubber is something which should be undertaken, not only with some prospect of production at a profit, but with the utility of such a plant as protection against unjustifiably high prices fully in mind. Factories for the production of synthetic camphor are ready to begin work whenever producers of natural camphor make it worth while. If the producers are wise, they will not tempt these plants to start operation. They stand as a safeguard for those who must buy camphor.

While the rubber growers seem to be well entrenched, it may be for their own good to remind them of the experience of the American distillers of hardwood. The advantage of natural raw materials has been largely lost through the fermentation process for acetone and acetic acid, the catalytic method for making acetic acid from acetylene, and now the synthesis of methanol, leaving wood charcoal alone without serious competition.

Rubber can be made by polymerizing butadiene and its derivatives. If the polymerization is carried out in the cold, a solid, inelastic material resembling bread is obtained; if carried out at 60° C., a rubber similar to natural rubber is formed. Both methods require several months to complete the reaction, but if the temperature is raised to 100° C. the reaction is apparently complete in a week or two, at least with small quantities. The Germans made both types during the war, starting out with 2,3-dimethylbutadiene. The cold polymerization product, known as "H" rubber, was successfully used for hard rubber articles, particularly submarine battery jars. The hot or warm polymerization product, known as "W" rubber, never came into extensive use. If vulcanized in the ordinary way it is "dead." Of course such a difference in vulcanization may be eliminated by further study, but it is very likely that this study will be long and difficult.

The Germans made their rubber from acetone, but nothing is known of the yield or the cost. Assuming that acetone can regularly be made for 10 cents per pound, even when very large amounts are in demand, and assuming that 50 per cent yields are obtained in each case, going from acetone to pinacone and thence to dimethylbutadiene, the materials cost of the latter would be approximately 40 cents, since the aluminium used for the reduction is quite inexpensive and no chemical reagent is used in the second transformation. The dehydration of the pinacone is carried out by distillation under pressure. If the polymerization is successful 50 cents per pound would not seem to be beyond reason.

Butadiene and its derivatives can also be obtained by cracking petroleum, and even by chemical treatment of butyl alcohol, amyl alcohol, etc. It would appear, therefore, that petroleum would be the cheapest source, and if the polymerized product could be made to vulcanize and give "live" products, that is where the emphasis should be laid.

The question of converting one basic commodity into another looms large as always. If the price of rubber stays up, sooner or later some synthetic rubber will be sure to make its appearance. It is difficult to tell how long the present price will prevail. It has been stated that plantations can produce rubber at as low a figure as 8 cents per pound, although the general opinion is that the ordinary production cost is something like twice that amount. At any rate, 25 cents per pound surely would cover production costs and a fair profit. Accordingly, synthetic rubber might have to meet this price in order to compete at all, except perhaps in very special places.

The business of reclaiming used rubber also suffered during the era of low prices, and under present conditions it is natural that the recovery plants should be enlarged and enjoy great activity. Here, too, is an opportunity for interesting and profitable research. It is no condemnation of reclaimed rubber to suggest that still better material of this sort is a possibility and, so far as statisticians can see, money invested in such research should prove a paying investment. Then there is always the question of good rubber substitutes and the design of compounds using reduced quantities of rubber.

We hear little talk of overproduction of a material of such universal use and for which new employment bears principally a direct relation to cost. These and other problems in this great industry of comparatively recent growth offer marked opportunities to those qualified by temperament, training, and experience to engage in research upon the most complex problems, for the synthesis of rubber is indeed a complex problem. It is not the rubber hydrocarbons themselves that present the greatest difficulty, but the nature of the latex particle itself. This is liquid, perhaps a mixture of three or four different hydrocarbons surrounded by the shell of other hydrocarbons, and this, in turn, by a film of nonrubber substances, principally proteins. This arrangement seems to be the same in all particles and their exact duplication is unquestionably difficult. However, other seemingly impossible problems, such as the synthesis of ammonia from inert nitrogen and hydrogen, have become accomplished facts and no scientist is prepared to admit that anything is ultimately impossible.

Although so far the raw materials have been too costly to make synthetic rubber a real competitor, continued high prices will be a challenge to the laboratory and one never knows from what test tube or from what catalytic bomb a revolutionary discovery may be brought forth.

Will the rubber industry make the discovery through coöperative research, will some progressive company undertake it on its own account, or will the opportunity be left to others outside the industry?

Modesty in Science

ON THE occasion of the Chemical Exposition, held now after a two-year recess, we are naturally inclined to call particular attention to the progress that has been made in the interim. Like other living things, chemistry and the chemical industry must grow or perish. In this number we have undertaken to present conservatively a few of the advances that have been made, and the Exposition itself will unquestionably point to many more in the Court of Chemical Achievement and in the booths of the many exhibitors. Recent times have been so filled with records of growth and achievement as to tempt boasting.

However, this seems a fitting place in which to emphasize the plea of Robert A. Millikan, made at the dinner of the AMERICAN CHEMICAL SOCIETY at the Los Angeles meeting. It takes a big man to be really meek, to display becoming modesty, and to be able to call upon others to learn the lessons of science and apply them to their own conduct. Dr. Millikan, a Nobel prize winner and one of America's foremost physicists, called for a greater display of modesty, noting points in the history of the last twenty-five years that should have taught us this virtue.

Unquestionably, that period has seen definite additions to our knowledge, but much that we thought we knew has now been proved untrue, and as we go forward with our work we are almost overwhelmed before the vast number of important things which we do not know. Scientists should be cautious in making general assertions and particularly careful to differentiate between experimental facts and mere speculations. One is safe in arguing from experimental facts which can be independently determined by other investigators, but unless care is taken to distinguish between these facts and the theories and speculations of the investigator, we may be led far astray. The theologian and the philosopher of the past could be accused of asserting knowledge where there was no knowledge. This cannot be forgiven in a scientist, and while we can point with justifiable pride to a substantial list of items under "Finished Business," the agenda under "Unfinished Business" is infinite by comparison. It behooves us to learn and practice modesty.

The Dean Passes

CHARLES FREDERICK CHANDLER, affectionately called "The Dean of American Chemists" and the "Nestor of Chemistry in America," has laid down an exceedingly active and useful life. He had earned his place in the chemical profession before many of us were born. He occupied a long list of honorable positions and was not only a charter and an honorary member but really one of the most active of the founders of the AMERICAN CHEMICAL SOCIETY. Both as teacher and consulting chemist he exercised a splendid influence on a long list of chemists who reacted to his stimulus.

Dr. Chandler had the privilege of living in one of the most interesting periods of the world's history and at a time when the changes in chemistry have been most far-reaching and rapid. Beginning as a pioneer in the teaching of chemistry and active in various matters pertaining to public health, he worked on into the period of synthetic chemistry and saw industry begin to take an interest in the type of work which the chemist can perform to its great advantage. He continued in productive work long after the age when most men retire.

The editorial comment in both the lay and technical press pays splendid tribute to this chemist who was interested in public affairs and the betterment of living conditions as well as in science. Beyond question here was a man who left a lasting impression.

Chemistry in Banking

THE advantages to the financial world which come from frequent consultation with chemists and chemical engineers have been thoroughly demonstrated abroad. Such contacts are mutually advantageous, and we have persistently endeavored to bring to the bankers of America such information as would enable them to decide to what extent it would pay to consult chemists frequently. The question has been discussed repeatedly with the secretaries of the state bankers' associations and with the national organization, with the result that both Dr. Teeple and Dr. Little have appeared before bankers' organizations under the sponsorship of the AMERICAN CHEMICAL SOCIETY and have delivered talks on "Research as a Basis for Credit" and "The Chemistry behind the Dollar." In concluding his address, Dr. Teeple said, "Given any chemical industry today, I would rather judge its future by its fixed attitude toward research than by its fixed assets, its working capital, or its past earning power." Dr. Little emphasized the point that "Financial audits, accounting, and appraisals are universally recognized as indispensable parts of the machinery of banking," but that "it is not yet generally appreciated that in very many cases chemical audits are equally essential and informing."

A few financiers regularly consult chemists before investing, and banking institutions have been known occasionally to turn to a specialist for scientific advice. It has remained for the Baltimore Trust Company to appoint upon its advisory board a consulting chemist and chemical engineer—A. E. Marshall of Baltimore. The appointment is made for serious work and Mr. Marshall's advice is regularly sought, with the result, we predict, that the bank will be more satisfied with its financial relations not only with chemical but with other industries.

The policy of having trained chemists upon financial boards is so sound that we believe we are doing the public a service in continuing to bring before bankers the desirability of such a course.

Lessons of the Shenandoah

THE country was genuinely shocked to learn of the disaster which overtook the Shenandoah and grieves for the men who lost their lives in the performance of duty. Yet it seems obvious that, however great our loss, we cannot simply wash our hands of aviation and decline to be further interested in aircraft of the lighter-than-air type. As is frequently emphasized, discovery, invention, and development constantly take their toll of human life and treasure. Progress is made only when the lessons of such disasters are well learned and applied.

Whatever investigation is made to ascertain the true cause of the disaster, it is doubtful whether good would come from printing all the details. It would be surprising if there were agreement as to the cause and certainly the data would be misinterpreted by many. After all, structures embodying our best designs and resting firmly on the earth are destroyed by windstorms and cyclones. It may never be possible to construct a giant dirigible capable of withstanding the stresses of the most violent storm or cyclone. Perhaps what is needed is better meteorological service to aid such ships to avoid storms.

The fatigue of metals is a subject little understood as yet, and reliable data are available on comparatively few metals and alloys. The frame of a dirigible must be subject to unnumbered alternate stresses. Something is known of the liability of aluminium alloys to corrosion, but this subject also affords ample opportunity for research. What protection can be given these alloys to arrest or avoid this destructive phenomenon? Surely it cannot be claimed that our knowledge of the metallurgy of aluminium alloys is anywhere near complete. These alloys are comparatively new. They have not been given the test of time in use, as have many of the older metals. While the utmost precautions were taken to test many duplicates of structural members of the Shenandoah and there is no charge of lack of caution in her construction, it would be a grave mistake not to study parts of the broken frame, resorting to every method of modern testing, particularly metallography. The etched polished surface under the microscope, which has played so great a part in many phases of modern metallurgy, may also help to find the cause of weakness if it exists in duralumin and point the way for avoidance in future.

The data which the full examination will disclose may give rise to extensive research in many fields where the specialists in several branches of the natural science must coöperate. Chemical, physical, mechanical problems abound. Their solution, bit by bit, will form a nucleus from which improved plans will be evolved.

Twelve Months of Progress

A Chemical Review of the Past Year

By D. H. Killeffer, Associate Editor

19 East 24th St., New York, N. Y.

WRITERS and speakers from the beginning of time have been inclined to discourse wisely on the constant flux of human affairs, the perpetual imminence of the dawn of a new era, and from their thoughts on this subject to deduce that the race stands on the brink of disaster or in sight of the promised land, according to their individual tastes. From the days of Tut-ankh-amen and before, such prophecies have been incontrovertible, for there never has been—and probably never will be, even if evolution is made unparliamentary—a time when civilization has not been changing in one way or another. There are many events of the past twelve months to which one may point with pride or which may be viewed with alarm. It is indeed difficult, if not impossible, to draw sane conclusions as to the trend of affairs from events so fresh in mind that they have not yet assumed their proper perspective in relation to all that have gone before, and it is far from our purpose to attempt prophecy. Yet the unformed future must be built upon the solid foundation of the past and it cannot be amiss to consider as dispassionately as may be some of the recent events which will go to make part of that foundation.

Court Decisions

As no picture is complete without a background, so it is impossible to confine the events here to be described within the definite time limits which have been set. Our first attention must be directed to the suit of the United States to recover the patents and copyrights sold by it to the Chemical Foundation as a result of the operation of the Trading with the Enemy Act passed by Congress during the war, for this possesses importance fundamental to our industry. This suit was brought by the Attorney General at the direction of President Harding on the basis that fraud had been committed in connection with the transfer of this property. It was decided in favor of the Foundation in the U. S. District Court, when Judge Morris on January 3, 1924, handed down a sweeping opinion upholding the Foundation in its every contention. The Government then entered an appeal. This was decided in the U. S. Circuit Court of Appeals, and an even more sweeping opinion in favor of the Foundation's contention handed down on March 26, 1925. The opinion of this court is one of the most interesting documents dealing officially with the relation of the industry and science of chemistry to the nation which has yet been published. It is official and thoughtful in a way impossible in a dissertation on this subject from those engaged in chemistry, and it is not involved in the complex terminology of either the law or the science with which it deals. Certainly, it should be carefully read by every loyal American.[1] The outcome of the appeal taken to the Supreme Court, the hearing of which has been set for November 2, may be awaited by American chemistry without misgiving.

The importance of this decision, as well as that which it affirms, can hardly be overestimated. Aside from the actual value to the industry of the patents involved, these two opinions point strikingly to the heavy responsibility which rests upon American chemistry in advancing our civilization. The views set forth in them are not new to chemists generally, but they are officially expressed in a way that places an obligation on the profession and the industry definitely to fulfil the promises and claims made for and by them. In no other way has chemistry's position in the scheme of things been so definitely stated by such thoughtful authority.

A Damage Suit

A verdict by a jury in Philadelphia in a suit brought against the Air Reduction Company by the Philadelphia Storage Battery Company, awarding damages to the latter on account of a fire caused by the failure of a faulty fitting sold to it by the former, sets a precedent in damage suits. The evidence was to the effect that the failure of a manifold supplied by the defendant for handling compressed oxygen caused a fire which destroyed the plaintiff's plant. The decision of the jury awarded $340,000 damages and thus set the precedent of allowing damages, not only for the value of the defective equipment, but for the total value of the property destroyed as well.

The Frasch Bequest

American agricultural chemists were much stirred last fall by the announcement that a fund of considerable magnitude (greatly exaggerated at the time) had been left in trust by the will of the late Elizabeth Blee Frasch, widow of Dr. Herman Frasch who made the mining of American sulfur commercial, for promoting agricultural chemical research in this country. The will provided that the fund should be administered by a trust company which should make grants from its income with the advice of the AMERICAN CHEMICAL SOCIETY, and stated that the residue of the estate, after certain comparatively small legacies had been deducted, should form the fund. Various rumors at the time placed the amount of this residue at as much as ten million dollars, but careful scrutiny of the estate by the executors has shown that it does not involve the estate of Dr. Frasch, which was previously disposed of, but only Mrs. Frasch's private fortune. The sum forming the trust seems to be not more than nine hundred thousand dollars, and even this is still subject to vicissitudes of litigation brought by the heirs attacking the legitimacy of the trust. Already the Surrogate's Court has passed upon the validity of the will and the original hearing in this court upheld the legality of the trust. An appeal has been taken from this decision to the Appelate Division of the Supreme Court of New York, and it is expected that the case will drag its weary course through all possible legal entanglements before any action can be taken toward carrying out the provisions of the will.

It is interesting to note that the conditions of the trust make grants possible only to incorporated institutions for periods of five years, at the end of which the work done shall be subject to review before a further grant for a similar period can be made to the same institution.

Foreign Developments

Intimately related to the matter of responsibility for the future has been the rapid development abroad, particularly in Germany, of processes and products which have no counter-

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[1] Available, gratis, from the Chemical Foundation, 67 Wall St., New York, N. Y.

parts here. American chemists have been a little too prone to consider that the war and the peace which followed had definitely transferred leadership in chemistry from Germany to this country, whereas American business has leaned the other way in believing that the opportunity had been reopened to it to reëstablish once lucrative connections with foreign sources. Both are partly right and both, very much wrong. The opportunity has certainly been opened to American chemistry, but leadership must be earned. At the same time American chemistry has gone much farther toward this goal than American business seems aware. Early in 1925 the importation of quantities of methanol produced from water gas in Germany at prices which threatened serious trouble, if not actual extinction, to our wood distillation industry caused much consternation among business men as well as chemists here. The importance of the particular process employed was greatly magnified and no cognizance taken of the fact that two very distinct advances had already been made in this country to counteract its effect. The efforts of the Germans in other directions—the hydrogenation of coal, an improved process for sulfuric acid manufacture, and active borrowing of American capital with which to buy their way back into American industrial life—have all met considerable success and have been disproportionately magnified by American business to the discredit of American scientific ingenuity. The situation is probably a much less serious blot on America's record of achievement than it seems, but nevertheless it brings directly home to us that we cannot long continue to ignore the activities of foreign investigators.

It must be recorded that the first importations of methanol, like the Germans' first gas attack in 1915, were somewhat premature and that the full weight of the threat cannot yet be realized. Just how soon this may come upon us is still a matter of surmise, but the operators of the process abroad have the obvious advantage of using, slightly changed, the old equipment of the Haber process plants. In the meantime the American wood distillation industry has been provided with a new process for operation on actual waste wood, which is said to be a great improvement over the old one, and an American consumer of large quantities of methanol has brought out a process for supplying his needs from natural gas, of which more later. Steps are also being taken to put the foreign process into operation here. The spur to American ingenuity which exists in the situation is certainly not being wasted and American business may well look closely into the details before passing hasty judgment.

Trade Associations

An increasing tendency on the part of the various groups allied to chemistry to organize for mutual help and the growing importance of the associations is to be noted during the past twelve months. Most of these organizations are older than a year, but their influence in matters of general trade interest is enormously greater. The old type of professional lobbyist is becoming less evident around legislative assemblies and is being rapidly replaced by the united voice of industry as represented with authority by its trade associations. Many groups have failed to realize this and the result has been unfortunate for them in a number of cases. The respect which legislators generally have for sound technical information and advice has been constantly growing as they have come into closer contact with able leaders in industry and with the Government's own scientists. It is gradually being borne in on the legislative mind that matters involving science or technology can best be understood, not by consulting corps of attorneys, but by going directly to experts in the particular fields. This growing importance of organized industry is largely the result of the good offices of the Secretary of Commerce, Mr. Hoover, and it represents a healthy trend both in coöperative research and in public relations.

An outstanding example of the effectiveness of thus uniting the opinions of industries is seen in the defeat of the so-called Crampton Bill in the last session of the Senate. This bill was designed to confer wide arbitrary powers upon the Prohibition Director and to minimize the control of the Treasury Department over industrial alcohol. In the fight against this measure the associations of the chemical and allied groups were effectively represented.

Prohibition Enforcement

As a more or less direct result of the disclosure at the hearings on this measure of the irksomeness to industry of the methods of the Prohibition Unit, a complete revision of the administration of the provisions of the Volstead Act has been undertaken. The direction of affairs has been put in the hands of Assistant Secretary of the Treasury Lincoln C. Andrews, an ex-army man. Included in his reorganized prohibition enforcement unit are all the former duties of that unit together with parts of the former duties of the Bureau of Internal Revenue and of the Coast Guard units devoted to the prevention of smuggling liquor. General Andrews has put himself definitely on record as favoring the industrial use of alcohol—a view which seemed entirely unacceptable under the old régime in spite of the clear statement of the law on the subject. He is further setting about the appointment of the twenty-two regional directors, whom his plan requires, with the apparent intention of selecting them from the highest type of men available in the country. It is altogether too early in the new régime to be able to express an opinion of any value, but the energy with which General Andrews is going about the gigantic task which confronts him and the definite stand favoring industry he has already taken justify a certain amount of hope. It is decidedly not a one-man job and industries as well as individuals must lend material aid to it if it is to be well and properly done. The eyes of the industry will be upon him and its help will be his to command so long as he does not indulge in the fanaticism which has previously characterized prohibition enforcement.

Muscle Shoals

The Ford offer for Muscle Shoals, which was so much the subject of discussion a year ago, was finally withdrawn after the failure of Congress to accept it in a time considered reasonable by Mr. Ford. After this withdrawal an effort was made in the House of Representatives to put the thing onto Mr. Ford's shoulders whether he would or not. The other bidders became again active in trying to persuade the property into their own hands and the whole proposition was so muddled by propaganda and counter-propaganda that the President, with the tardy approval of Congress, very wisely appointed a commission to consider and weigh carefully all points in question to enable it to advise properly as to the disposition of the property—a step which President Coolidge advocated in his first message to Congress two years ago. On this commission were appointed former Representative McKenzie of Illinois, former Senator Dial of South Carolina, Prof. Harry A. Curtis of Yale University, William McClellan of New York, and Russell F. Bower of the American Farm Bureau Federation. The report of this commission has been asked before the convening of the next session of Congress in December, and it is hoped that this will clear up the now beclouded situation and make possible a proper use of this white elephant.

Transfer of Government Departments

During the year the Bureau of Mines and the Patent Office were transferred from the Department of the Interior, where they did not logically belong, to the Department of Commerce, where they can be more efficiently administered. Probably the most important effect of the change was the direct result of the close coöperation which exists between the Department of Commerce and the business world, and consisted in the appointment of a technical committee advisory to the Bureau of Mines. The excellent work of this bureau at its Pittsburgh station, in the cryogenic investigations in Washington, in the development of helium for commercial aviation purposes, and in its other endeavors is receiving added impetus from the assistance thus afforded it from leading thinkers in its field.

The improvement in administration in the Patent Office has been largely in added efficiency in handling patent applications and in vigorously carrying on the efforts to reduce the time between the filing of an application and its review by the examiner, a move initiated before the transfer. As a result of this policy, the Commissioner of Patents reported on July 31, 1925, that the oldest application then on file which had not been reviewed was dated February 14, 1925. This compares with an interval between July 25, 1924, and November 12, 1923, and between July 27, 1923, and September 26, 1922, one and two years ago, respectively. Both transfers have the hearty approval of those most affected.

Motor Fuel

Following the Teapot Dome investigations President Coolidge appointed a Federal oil conservation board made up of the Secretaries of the Interior, War, Navy, and Commerce. This board has been studying the situation in our oil supply with due regard to possible substitutes, and it is expected that their findings and their continued action will operate to prolong the present supply of oil and prevent the possible recurrence of the recent scandals.

The attention of the whole country was directed forcibly to the question of possible health hazard from tetraethyl lead last October, when a number of workmen in the plant of the Standard Oil Company of New Jersey were seriously poisoned while making this material. The hysteria that followed the death of five of these men culminated in a voluntary withdrawal, by the manufacturers, of gasoline treated with tetraethyl lead from the market until such a time as a committee of seven appointed by the Surgeon General of the United States shall make its recommendations. This committee is actively engaged in determining the true status of this valuable ingredient of motor fuel and is expected to report findings about the first of the year. Opinion has been sharply divided as to whether or not there exists a real hazard to the public health in the use of such fuel, and it is hoped that the investigations now on foot will resolve the differences.

In the meantime several other remedies for knocking in gasoline motors have been brought out, based largely on highly cracked gasoline. It was known that unsaturated hydrocarbons reduce knocking in ordinary motors, but it has not been proved that they offer anything like the efficiency of tetraethyl lead in high compression motors, which it will be necessary to use to gain any really considerable benefit from antiknock compounds. The search for other possible substitutes for the lead compound which might accomplish the same thing without health hazard is being vigorously prosecuted, but no compound has yet been found which is comparable with lead's efficiency.

Deep Sea Chemistry

In connection with the stringent shortage of bromine and its compounds caused by the early commercial development of tetraethyl lead, a revolutionary process for the extraction from sea water of its minute bromine content was devised and successfully operated for a short time. The plant for accomplishing this was mounted on one of the Shipping Board's freight fleet, and in view of its revolutionary character and the wide publicity given it at the time the opinion was variously expressed that the entire thing was a gigantic hoax perpetrated merely as a publicity stunt. This was not the case. The vessel made one voyage returning with recovered bromine in satisfactory quantity just at the time tetraethyl lead was withdrawn from the market, which accounts for the fact that it has not undertaken subsequent voyages. The process consists in releasing bromine from the sea water by chlorine and subsequently precipitating it as tribromoaniline, which is directly usable in the treatment of gasoline with the lead compound. In order to carry out the process efficiently—15,000 parts of sea water contain about one part of bromine—it was necessary to assure a ready supply of pure sea water at as low pumping cost as practicable. This led to the development of apparatus for carrying out the reactions continuously on board a ship. No official report of the first voyage of this unique chemical ship has yet been made public, but it is understood unofficially that the hopes of her operators were fully realized and that the process is reasonably economical for the production of this particular organic compound and of combined bromine, if it can be used in this form.

It is interesting to note in this connection that German investigators have devised a process, which they report has succeeded on a laboratory scale, for the extraction of gold from sea water. The process involves the absorption of gold by silver sulfide. Whether this process will ever become commercial cannot be foretold at the present stage of the proceedings, but if it does we may then look forward to the shattering of that other fallacy, amusing to generations of chemists, the bottling of sunshine and its extraction from cucumbers.

The continued successes of various German and Japanese investigators in transmuting mercury to gold have attracted wide interest, but all efforts to duplicate their results in this country have so far failed to produce detectable quantities of the precious metal. This transmutation is still far from profitable and there is no indication yet that it ever will be so.

Chemical Warfare

During the year Congress has recognized the Chemical Warfare Service as a distinct and important part of our army organization by appointing its chief Major General. This places the chemical branch of the service on a par with the artillery, infantry, and other arms. Perhaps because and perhaps in spite of this, the service has been selected by the pacifist organizations of the country as the most vulnerable point of attack in putting over their ideas of disarmament. To counteract their propaganda a Chemical Warfare Association has been formed and is expected to function by organizing the opinion of the chemical profession and the reserve officers of the service in much the same way that the infantry and artillery associations do those interested in their arms.

The exact status of chemical warfare in international affairs has been so beclouded by pacifistic propaganda that it may be well worth while to review it here. The Washington Limitation of Armament Conference, against the advice of its committee on the subject whose report was carefully disregarded and suppressed, adopted a treaty in 1921 barring the use of chemical weapons between the signatory powers. This treaty was to become operative and binding on the signers only after all ratifications had been deposited at Washington. None of these ratifications has yet been deposited and hence this treaty is not binding upon anyone, France having refused to accept it. Representative Burton, at an international conference on traffic in arms at Geneva this year, spoke eloquently, if uninformedly, for this country against international trade in war chemicals and made an opportunity for the introduction of a resolution banning chemical warfare methods. The German representative seized the opportunity and loudly proclaimed the desire of his country to be the first to sign such an international agreement. The motive behind this move on Germany's part to disarm the rest of the world chemically is worthy of a Hohenzollern! An effort will probably be made to obtain ratification of this agreement in the Senate during the forthcoming session of Congress. It has the whole-hearted support of all pacifists, who expect to be able to put the ratification through unnoticed on the basis that it is merely the restatement of the stand of the Washington Conference of 1921. The responsibility of leadership in the movement to prevent this, and with it the recurrence of the horrors of Ypres on April 22, 1915, rests definitely upon the chemists of the country, who realize fully, as no one else can, the dangers of unpreparedness in the face of a breach of such a treaty.

No small part of the argument advanced against the use of chemical methods in warfare is based upon a complete misunderstanding of them. The official records show that deaths from gas in the Great War were far fewer in proportion to the total casualties than was the case with the other weapons. The efficiency of gas lies in the temporary disability of the soldier exposed and in a vanishingly small proportion of the cases of gas casualties has there been any permanent effect on the man. Gas does not cause tuberculosis or any other disease of the respiratory system, nor does it render the soldier more easily susceptible to such diseases, according to the testimony of members of the Medical Corps before the committee investigating the affairs of the Veterans Bureau. Comparatively few of the chemical agents used in warfare are definitely toxic, but they are rather designed to hamper seriously the activities of troops through the use of smoke screens, lachrymators, sneezing gases, vesicants, and the like, which obscure the vision or destroy morale. The smoke screen is too valuable in war to permit its abandonment, yet this harmless chemical weapon is sought to be banned with others. Certainly, a proper understanding of the casualty reports of the late war from all nations points to both the humanity and efficiency of this type of weapon. The chemists of the country must consider themselves individually responsible for the misunderstanding of their arm of the national defense and set about to correct it.

It is interesting to note that criminals are following war methods closely and that several have conducted robberies during the year by the use of chemical arms. Similarly, a number of robberies have been effectively prevented by tear gas.

Organic Chemical Advances

The synthetic organic chemical industry has not prospered so well as other branches of chemistry. During September, 1924, an automatic reduction in the duty levied on synthetics went into effect under the tariff act. This act provided original duties of 60 per cent ad valorem and 7 cents per pound on finished products and of 55 per cent and 7 cents per pound on intermediates. The reduction brought these to 45 per cent and 40 per cent, respectively, retaining the specific duty of 7 cents per pound. The effect of this reduced duty was an immediate striking increase in the imports of dyes. The figures of the Department of Commerce show imports of dyes and coal-tar products amounting to 1,215,959 pounds, valued at $1,234,884, during the first six months of 1924 as compared to 2,503,151 pounds, valued at $2,320,844, for the corresponding period in 1925. The figures for value here given were made up before payment of duty and hence indicate that it is now possible to import dyes of lower average value. There is also in progress abroad gradual progressive reduction in the cost of manufacture. This branch of the industry has been active in supplying to the Treasury Department a complete set of standard samples of new dyes for comparison purposes, as the duty on dyes is levied entirely upon the basis of tinctorial value as compared with the lowest commercial strength of the same dye. The American valuation provision of the clauses in the tariff act dealing with synthetic organic chemicals, as well as the decisions of the customs appraisers made under it, has been upheld in the courts.

New Dyes

During the eight months ending June 15, 1925, thirty-six new dyes were produced in American plants. Among these were many vat dyes, so important on account of their great fastness, and a complete line (twelve) of new dyes for printing cotton without either fore- or after-treatment. They obviate the necessity of mordanting, after-chroming, and all similar treatments, and simply require to be printed directly upon the fabric from rolls or blocks. They mark a distinct advance in the art of dyeing which is directly creditable to the American dye industry and have no counterparts in the lines of other countries. Included in this list of new dyes made here are a number especially for dyeing acetate silks, a peculiarly difficult problem.

From Scotland comes the news of the development there of soluble vat colors based on indigo sol. These dyes are derived from anthraquinone and are applied as direct colors but give the properties of vat dyes on the fiber.

A new German product somewhat similar to a dye renders the fabric to which it is applied completely and permanently immune to destruction by moths. Dyeing with it may be accomplished in a padding machine or in a regular dye bath. About one per cent is applied to the wool after dyeing and fulling have been completed as it is removed by such operations. For material other than piece goods, such as carpets, upholstery, and so on, the treatment may be sprayed on. It is colorless, odorless, and nonpoisonous to human beings. It is fast to dry cleaning and steaming operations and is permanent except when the goods are washed or re-dyed.

New Medicinals

As this is being written the announcement by two British investigators of the isolation of a microörganism related to cancer which may possibly be its definite cause—although there is much discussion of this point—is still occupying much space in the daily papers of the world. Although items about this remarkable piece of work are now appearing on the inside instead of the front pages of the press, the world is still thrilled by it and by the possibilities which it seems to place in prospect of a specific cure for this dread scourge of our race. Great care has been exercised to prevent the false hope that a cure is already available, but it is confidently hoped by everyone that this care may soon be made unnecessary by the discovery of the needed specific. If it should prove that this microörganism is responsible for human cancer, there is a possibility—nothing more than a possibility—that the recent development of new antiseptic agents may lead to the key to this problem as it has to the cure of septic poisonings. The efficacy of a sodium-gold salt, called sanocrysin, in the cure of tuberculosis has been reported from Denmark. Clinical tests carried out there indicate a very considerable curative value for this material, but physicians in this country are awaiting further proof before accepting the new remedy as a cure.

Hexylresorcinol (*n*-hexyl-2,4-dihydroxybenzene) has been shown during the past year to possess remarkable efficiency as a germicide, while having no deleterious effect upon the human body. It has been developed from a laboratory curiosity to a commercial product, generally available, and in such great demand that its manufacturers are having difficulties with unfilled orders, within the short space of six months. Its phenol coefficient—its efficiency in killing bacteria as compared with that of phenol—is between 45.0 and 55.0; yet it may be taken internally in doses as large as 0.6 gram three or four times a day without injury. It is excreted in the urine unchanged and thus creates a germicidal condition in the entire urinary tract. It has special value in the treatment of nephritis and other septic conditions in the bladder and kidneys. For this purpose, as well as for the treatment of certain infections of the digestive tract, hexylresorcinol has been remarkably successful. Micrococci and colon bacilli yield readily to it without the necessity for other treatments. It was developed by Dr. Veader Leonard at Johns Hopkins University.

Investigations on the bacteriostatic action of certain dyes, which seem to have distinct selective action, have been productive of much good. The dye itself, injected in solution, seems to enter into combination with parts of the bacterial cell and prevent its reproduction. This treatment has been successfully applied to infections of the pleural cavity and the results so far attained lead to the belief that this technic may result in the conquest of still other diseases now regarded as incurable.

Insulin has been on the market for some time now and is in wide successful use by the medical profession. Further investigations of its nature are being vigorously prosecuted and according to a recent announcement a marked increase in its activity has been obtained through fractionation. The work has been carried on at Johns Hopkins Univerisity by Drs. John J. Abel and E. M. K. Geiling. The fact that a fractionation of the commercial product, derived from animal pancreases, can be accomplished in such a way as to increase its activity many fold leads these investigators to believe that a pure chemical compound, responsible for its activity, may possibly be isolated and later synthesized. During the course of the investigation the further interesting observation was made that the active fraction contains less phosphorus and more sulfur than the original. It would seem from this that a new relation between the hitherto neglected sulfur content of the food and diabetes melitus may be discovered which would upset present theories of the disease.

Solvents

The synthesis of methanol from water gas has already been mentioned. The process used is subject to a number of patents, over which there is the prospect of litigation, but it is quite simple from a chemical point of view. A mixture of carbon monoxide and hydrogen under pressure is passed over a suitable catalyst at a high temperature. The resulting mixture contains a large percentage of methanol together with other related compounds, alcohols, hydrocarbons, and acetone. The catalysts apparently employed are zinc oxide containing small amounts of copper and a cerium aluminate with which finely divided nickel is mixed. Others are claimed in the various patents, but these two seem to be preferred. Descriptions of the process and its effect on American affairs have been published.[2]

To meet the situation thus created two recent new developments by American chemists are important. The Stafford process for wood distillation, a continuous process in which finely divided wood may be used and which operates by utilizing the exothermic reaction of carbonization to initiate further carbonization, is already in successful operation in this country. In addition to this, the manufacturers of phenol-formaldehyde resins have recently announced new processes by which they hope to supply their large requirements of formaldehyde. This affects the methanol situation directly, as formaldehyde is made from methanol and this industry is one of the largest users of this particular product. The new processes are based on the chlorination of methane from natural gas to methyl chloride and dichloride. From the first, methanol is made direct, and from the second, hexamethylenetetramine may be made for direct use in making plastics. It has also been found possible to manufacture satisfactory plastics using methylene dichloride to replace formaldehyde. These two developments show convincingly that American chemists have not been caught asleep by the new German development, as many who have not investigated the situation have erroneously supposed.

The synthesis of isopropyl alcohol from the waste gases of petroleum cracking has been put into wider use during the year and improvements in the process have been developed. Synthetic butanol from acetylene has been rumored on several occasions, but has yet been only a rumor so far as American commercial production is concerned. Research looking to this development is being actively prosecuted, but it is still a laboratory matter.

Tetralin (tetrahydronaphthalene) and hexalin (hexahydrophenol), solvents first produced in Germany during the war years to eke out the supply of turpentine and its substitutes and to enlarge the supply of motor fuel, are now being produced in this country in considerable quantities and at prices which make their use in American industry practicable.

Tetralin is a stable, water-white liquid with a specific gravity of 0.975 and a boiling point 204° C. It was developed as a substitute for turpentine, particularly for use in paints. It has a remarkable solvent action on gums, oils, and waxes, and can only be used in paints which are sprayed on owing to its high solvent action on linoxyn. In addition to its use in paints, tetralin was extremely valuable to the Germans in admixture to benzene and alcohol as a motor fuel. A combination of 60 per cent benzene, 30 per cent alcohol, and 10 per cent tetralin was found extremely satisfactory as a motor fuel. The solvent action of tetralin, its high boiling point and low volatility, make it most valuable as an ingredient of detergents containing small quantities of hexalin as an emulsifier and a soluble oil. It is available from American manufacturers in quantity at 20 cents per pound in single drum lots, which makes it possible as a raw material for many operations.

Hexalin is an oily, water-white, stable liquid with a specific gravity of 0.945 and a boiling point of 160° C. Its principal uses are as an emulsifier in detergents and as a solvent for a wide range of gums, waxes, rubber, and nitrocellulose. It is particularly important as an addition to the ordinary volatile solvents used in nitrocellulose lacquers on account of its comparatively low volatility. Three to five per cent of hexalin added to the lower boiling solvents used in lacquers produces a film of high gloss which will not blush under the most severe conditions and which flows much more smoothly than the ordinary ones. It is to be had at 60 cents per pound in single drums, and hence is not out of commercial reach.

The manufacture of these two solvents has required the construction of a complete modern hydrogenation plant. To carry out the reactions involved in their manufacture the raw materials—phenol, naphthalene, and hydrogen—must be of extreme purity, and hence special purification apparatus has been devised. The plant for producing these solvents has a capacity of approximately 100 tons per month and provision has been made for fourfold expansion of this if necessary.

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[2] This Journal, 17, 430, 859, 981 (1925). See also This Journal, News Edition, issue of June 20, 1925, p. 3.

Hydrocyanic Acid Fumigation

Many deaths from the use of hydrocyanic acid in fumigating have led the City of New York to ban its use. The comparative ease with which this operation might be made safe by the addition of a tear or sneezing gas has apparently escaped the disinfectors. Undoubtedly, some such addition to their technic will be required if they are to continue in business.

Carbon Monoxide Poisoning

The increasing congestion of motor traffic in our cities is resulting in what threatens to become a serious situation with respect to pollution of the air by carbon monoxide. Many surmises have been made on this subject, and much serious study is being devoted to methods of determining and avoiding dangerous accumulation of the poison in our atmosphere. In the meantime many "go-getters" are using the fear which constant reports of deaths from carbon monoxide in closed spaces engender to aid them in marketing all manner of trick appliances to obviate danger. Many of these are quite as ineffective as one that was said to filter out the poisonous monoxide molecules on a fibrous filter medium and let the other harmless ones pass!

An unexpected advance in the methods of treating serious carbon monoxide poisoning and other similar cases where collapse follows accidents has come from the discovery that a small amount of carbon dioxide mixed with the oxygen given the patient aids breathing materially. Several theories have been advanced to explain this phenomenon, but, whether it be explained or not, the fact remains that much quicker and surer recovery from collapse from carbon monoxide, electric shock, drowning, and similar causes in which breathing stops is noted universally when carbon dioxide is mixed with the oxygen. So definite have been the results of exhaustive tests that the City of New York and many of the large coal-gas works have made the equipment for administering this gas mixture a part of their regular first aid outfits.

Helium and Compressed Air Colic

In a similar way the surprising observation has been made that helium mixed with oxygen may be used to replace air in compressed-air caissons and that this synthetic atmosphere largely obviates the danger to caisson workers of compressed air colic, or caisson disease. Just why this should be so is not yet well understood, but in such an atmosphere it is possible to reduce or increase the pressure upon the worker at a much faster rate than with air without danger to him. It is expected that this will greatly extend the range of tunneling and salvaging operations where they must be conducted under great pressures.

Selenium for Flameproofing

A remarkable property of elementary selenium, although itself completely combustible, in almost completely flameproofing insulation on electric wires has been discovered during the year. A kilogram of selenium applied to the cotton insulation on No. 22 switchboard wire renders two miles of this flameproof. The desideratum in this case is that the insulation cease to burn when the igniting flame is removed. This has been achieved by even this minute amount of selenium, whose action is so successful that a treated wire will flameproof several untreated ones wound into a bundle with it. According to those who have investigated it, this action seems to be in some remarkable way connected with the smothering of the flames by the flammable selenium vapor.[3]

Lacquer Developments

A year ago the effect of the development of cellulose lacquers on the paint industry and on automobile finishes was discussed.[4] We have now to report that these lacquers are finding constantly new uses, the most recent of which is for finishing furniture. One firm engaged in lacquer manufacture has developed its product to the point where the retail buyer may obtain a variety of lacquers put up in household packages at the regular paint stores, and another is actively advertising to the furniture manufacturers.

Nitrogen Fixation

Although it is extremely difficult to divert the popular mind from the idea that Muscle Shoals can only be utilized for the production of cheap fertilizer—the watchword of the campaigns to capture this property—yet there seems to be no present doubt that such a use for this power would be little short of foolhardy. The development of various synthetic ammonia processes has reached too high a point to permit of its economical use for nitrogen fixation. During the year construction has been started of a plant for the application of the Claude process in this country. This plant will have a capacity of 25 tons of ammonia per day. The several processes operated in plants already built in this country are producing more than 50 tons of ammonia per day, and it is expected that expansion now under way will shortly bring this figure up to nearly 100 tons. Already more than half a dozen processes, or rather mechanical modifications of the same fundamental process of bringing about the combination of nitrogen and hydrogen by high pressure and temperature in the presence of a catalyst, are in operation in the United States.

Acetic Acid

Synthetic acetic acid is to be produced shortly by a new combination of companies operating in Niagara Falls, N. Y. Although the tariff on acetic was designed to protect the wood distillation industry, it is actually operating to bring this synthetic industry into the country where the tariff will protect it as well. The plants to be erected are to have a capacity fully equal to the growing demands for this product from the solvent industries, and the effect on the wood distillation industry of this renewed attack on its former monopoly is becoming serious.

Rubber Prices

During the past few months prices of crude rubber in all markets have fluctuated alarmingly as a result of the operation of the so-called Stevenson plan for the control of rubber exports from the British colonies. This plan—devised by a committee of eight appointed by the British Secretary of State for the Colonies to consider remedies for the rubber depression of 1921 and 1922, and of which Sir James Stevenson was chairman—became operative on the first of November, 1922, and provided prohibitive export duties on all crude rubber exported from the Federated Malay States, Straits Settlements, and Ceylon above the amount determined by a sliding scale based on the selling price in London. Although not compulsory upon them, British planters elsewhere followed the schedule of exports as a matter of policy. The situation which it was sought to correct by this plan had its beginning in the depression of business throughout the world during 1921 and 1922, but the difficulties caused by this were greatly aggravated by the fact that many young plantations—planted five or six years before, during the rubber shortage

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[3] This Journal, 17, 163 (1925).

[4] This Journal, 16, 995 (1924).

caused by the war—had just come into bearing during 1920 and 1921. The resulting overproduction of crude rubber caused the planters' selling price to drop below production cost and this seriously threatened the rubber industry.

The Stevenson plan to correct this situation is based on a graduated tax upon all exports of crude rubber above an amount determined beforehand. Each estate's capacity for production was estimated and beginning with the first of November, 1922, exports from that estate at the minimum tax rate were permitted only up to 60 per cent of this rated capacity. Above that amount the tax became prohibitive. According to the plan this rate of export was to be maintained for a period of 3 months, after which it was to be automatically revised according to the price of crude rubber in London. If this price averaged between 1 s. 3 d. and 1 s. 6 d. during the quarter, an increase to 65 per cent was to be permitted during the subsequent quarter. Similarly, if the average price was greater than 1 s. 8 d., the increase was to be twice as much, permitting 70 per cent of capacity to be exported during the subsequent period, and so on. If, on the contrary, rubber prices declined below a shilling per pound, an automatic reduction of 5 per cent was to be made from the quantity exportable at the minimum duty. If this scheme had been successful in keeping the price of rubber above 1 s. 8 d. for one year from November, 1922, all restrictions would then have been removed, or if the price had remained between 1 s. 3 d. and 1 s. 6 d. for two years the restrictions would have become inoperative at the end of that period. This was not the case, however, because rubber stocks throughout the world amounted to 110,000 tons in January, 1922, on which the rubber industry had drawn to the extent of 98,000 tons by April 1, 1925. During the period from November, 1922, to April, 1925, prices in New York—closely related to London figures—actually fluctuated on this account between a low figure of $16^{1}/_{4}$ cents per pound and a high one of 37 cents per pound, which naturally set the expansion of exports back very considerably from the maximum possible under the plan.

During the spring of this year the building of automobiles was carried out at 35 to 40 per cent greater production than was originally scheduled. Since automobile tires consume about 80 per cent of the world's rubber, this made an entirely unexpected drain on the dwindling stocks which it has been impossible to offset quickly by increasing production in the East. By the first of July, 1925, all the rubber reserves had been consumed and prices began to skyrocket, rising to a maximum of $1.24 per pound in the New York market at one time during the month that followed. Although there does not now exist any actual shortage of rubber in the world, an apparent one has been made possible by the fact that shipment from plantations require about three months to reach consuming centers. A few months may be expected to bring about a proper readjustment of affairs without further trouble.

American Efforts to Grow Rubber

Investigations by the Department of Commerce of the growing of rubber and close coöperation with industry on the subject have resulted in the taking of steps by American rubber manufacturers to set out plantations of their own rather than to depend on foreign-owned sources of supply. One American firm has been carrying on extensive experiments in Liberia and has recently announced that it will expand its plantations to cover a million acres there. This development is particularly interesting as showing the results to be accomplished by the coöperation of government departments and industry, and it is expected that others along the same line will follow.

Industrial Power

In our review last year the development of a mercury vapor boiler for power purposes was mentioned.[4] This year an even more startling device has come to light. An internal combustion boiler in which the gaseous fuel is burned in actual contact with the water in it has been put into successful operation in England on a fairly large scale. So revolutionary, and apparently so impossible, an idea as 100 per cent utilization of the heating value of fuel in a boiler has actually been accomplished by this means. Our entire conception of evaporation and power generation may have to be revised on this account. In addition, it has been found that much greater efficiencies are achieved by generating steam under critical conditions than have hitherto been possible under ordinary conditions. The whole trend of steam power thought has been toward higher and higher pressures and temperatures, and the results of British investigators indicate that sharp increase in efficiency is attained at 365° C. and 194.6 atmospheres (the critical points for water).

New Elements

Two new elements have been discovered during the year by the use of X-ray spectra. These have been called masurium (Ma) and rhenium (Re), and occupy positions 43 and 75 in the periodic system. These elements were discovered in columbite by German investigators, and their presence in the periodic table leaves only three probable vacancies to be filled.

Questionable Developments

Fakes are always to be found on the fringes of science utilizing the earnest work of research laboratories for coaxing the unwary dollar from the innocent bystander. The announcement by the Post Office Department that the use of the mails had been denied the Burnham Chemical Company, supposedly engaged in the exploitation of American potash and for that purpose accumulating much unprotected capital, places a period to its activities. The announcement here a year ago of the synthesis of sugar by E. C. C. Baly in Liverpool was immediately followed by efforts on the part of certain fakers to promote a company for doing this commercially. The symposium on corrosion before the AMERICAN CHEMICAL SOCIETY's Baltimore meeting attracted much favorable public notice and on this account was immediately followed by efforts to capitalize this publicity for the promotion of an asphalt base paint, which was claimed to be "breathed into the pores of the metal" and thus render it permanently resistant to all chemical agencies including "hydrofloic acid." A process for the commercial extraction of gold from rocks in which ordinary assays failed to find a trace of it has come in for court scrutiny, with the result that a ban has been placed on the sale of the stock of the company promoting it.

Tenth Revision of Pharmacopeia Available

The Tenth Revision of the United States Pharmacopeia, which is now off the press, contains many new drug standards which will become effective January 1, 1926. The Pharmacopeia, which is being translated into Spanish for use in Spanish-speaking countries, contains the following announcement:

> Biological assays have now been made compulsory for a number of important drugs and preparations, and in order to facilitate the adoption of these standards and to provide a greater degree of uniformity in the application of these assays, the officials of the Bureau of Chemistry of the U. S. Department of Agriculture, Washington, have indicated their willingness to supply substances conforming to the new pharmacopeial standards.

The use of these standards is optional, however, but it seems fair to assume that they will be made the basis of comparison by all manufacturers.

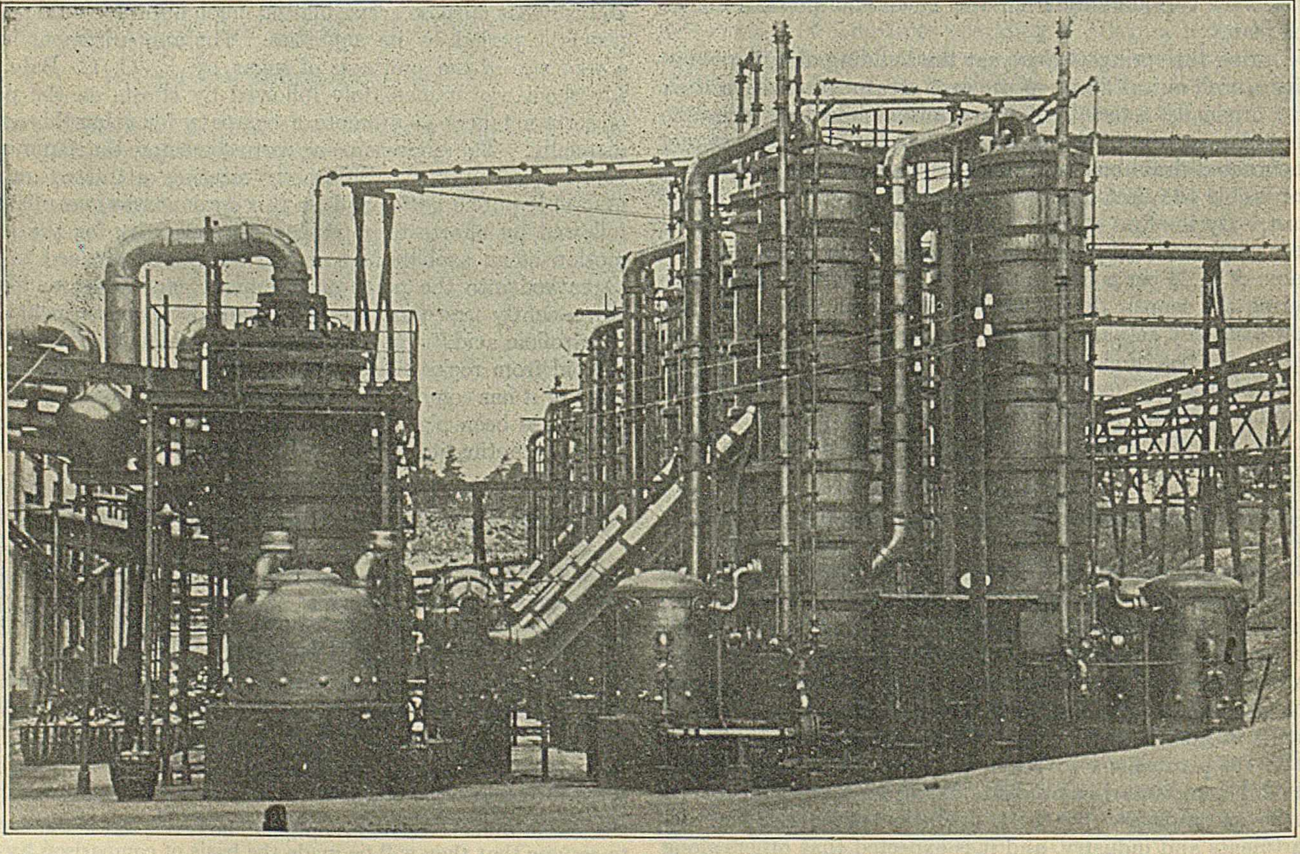
Progress in Chemical Equipment

Accomplishments in Chemical Engineering Equipment since 1923. Reported through the Chemical Equipment Association by Its Members

INDUSTRY'S advances seldom occur with the suddenness of inspiration. They do not, like Minerva, "spring full-armed from the brain of Jove." Rather they are the result of long processes of slow growth and painful development of multitudes of inspirations. Friar Bacon, pondering centuries ago in a monastery in medieval Europe, conceived of ships propelled without oars, and of machines by which men might fly like birds. He might very well have given the world these modern conveniences, had he only been provided with the mechanical means to clothe his ideas. Yet these philosophic dreams did not become realities until Fulton, backed by the discoveries and inspirations of centuries of investigators, launched the Clermont, and the Wrights, similarly fortified by the labors of countless students of mechanics, flew in their first heavier-than-air flying machines. Advances of civilization depend upon accumulated ability for accomplishment to no less a degree than upon brilliant inspiration.

Thus one may profitably look upon the improvements made in the tools of an industry as a more or less definite index of the direction which its further progress may take and of the extent to which it may be reasonably expected to go forward. We of the chemical industry, particularly, can survey with profit the activities of the manufacturers of the tools of our trade, for we are completely dependent upon them for necessary assistance in putting our ideas to work.

We shall find much that is entirely new in such a survey, despite the lack of any general stimulus to this field by the chemical industry during the past few years. Business for the chemical manufacturer has been regular, steady, and reasonably profitable. The goad to feverish activity which existed during the war years and those immediately following has not affected the situation of the past few years perceptibly. After the collapse of the post-war boom most manufacturers found themselves harnessed with hastily built, more or less inefficient plants and set about at once to effect those economies in all their operations which represented profit in the subsequent period of keen competition. These necessary savings have been brought about more by the improvement of the minutiae of plant equipment than by the scrapping and replacement of usable apparatus by distinctly new and better forms. It is true that some processes have had to be revised completely and new plants built to accommodate the alterations, but this has been the exception rather than the rule in the industry. We find equipment manufacturers busying themselves most largely with the production of more efficient fittings and apparatus to meet the needs of their clients in the face of highly competitive markets for chemical products, and in this a few new forms have been introduced. In general, too, the problem of the equipment manufacturer has been one of supplying replacements for worn-out and inefficient parts rather than of assisting with the building of new industries. From such a point of view, the accomplishments of the past two years or so show steady advances in the industry, and point the way to continued progress.



Complex Stoneware Installation for Hydrochloric Acid Manufacture Built by the General Ceramics Company

Catalytic Gas Reactions

The rapid development abroad of catalytic gas reactions has been keenly felt in this country, notably in the synthesis of ammonia and of hydrocarbon compounds from water gas. Efforts to put these and similar reactions to work in this country are being made in many directions. Indeed, the synthesis of ammonia by the Haber and other processes has been in operation in this country for a number of years and the development of the Claude process here is expected soon to result in commercial production. Just what form the synthesis of methanol and related compounds from water gas will take is difficult to determine at the present stage of things, but the methods used in ammonia synthesis will undoubtedly be modified to meet the conditions of these reactions. However, such processes, on account of the great expense of installations for handling gases at high temperatures and pressures, cannot be of sufficiently wide application, in the near future at least, to justify equipment manufacturers in standardizing the special apparatus required. Perhaps the next few years will lead to such developments, but they are still below the horizon.

It is of particular interest to note in this connection that wood distillers have already been supplied with a new process which bids fair to compete with the synthetic processes that have been progressively invading their field. They have long been working under the handicap of being compelled to use wood in the form of logs rather than the miscellaneous wastes of lumbering. This has forced the industry to compete to some extent with other users of timber for its raw material and, coupled with the fact that even this wood has had to be kept a number of years for seasoning, has been a great burden of expense to its operations. The difficulty in using waste wood has been largely one of retort capacity and heat transfer and has been overcome by the development of a continuous process which utilizes the heat given off by the exothermic reaction of carbonization. The success which this process has already met leads one to hope that by thus using an actual waste product of nuisance value the industry of wood distillation may be able to survive, in a modified form perhaps, the competition of the progressive development of synthetic processes.

Acid Resistant Materials

The problem of corrosion resistance is met in every branch of the chemical industry and its solution is of first magnitude in the operation of chemical plants. Stoneware, glass, metals resistant to corrosion, and coatings of various kinds play important parts in every kind of chemical activity. In each of these fields advances have been made during the period under consideration.

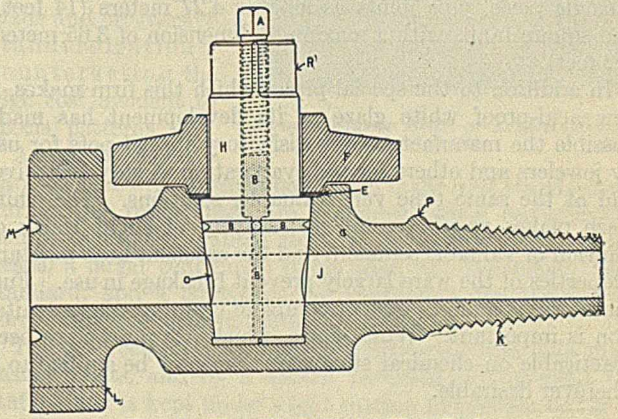
Large Stoneware Tanks

Increasing use of stoneware has led to demands for larger and larger tanks until a point has been reached where it is no longer possible or economical to manufacture them in a single piece. Such one-piece vessels are available up to 4500 liters capacity (1200 gallons), but even these fail to meet the demands for larger sizes. To meet this situation, built-up tanks consisting of an outer retaining wall of reënforced concrete, common building brick, steel, lead, or other convenient material lined throughout with acid-proof brick laid in acid-proof cement are being largely used. The service to be expected from these tanks depends primarily upon the properties of the brick lining and of the cement with which it is held together. Cements developed for use with acid-proof stoneware brick have shown remarkable resistance to the most corrosive solutions. A notable instance of the excellence of this construction is found in a pickling tank installed by Maurice A. Knight in the works of the International Nickel Company, at Huntington, W. Va. The pickle solution employed there for pickling monel metal, itself an acid resistant, consists of concentrated sulfuric acid, concentrated nitric acid, and a salt in combination at or near the boiling point. Even under these most severe conditions after more than a year of service the acid-proof brick and cement tank has been completely satisfactory. Many other installations of a similar nature are equally efficient in service.

Chemical stoneware laboratory sinks, drains, and vent lines are becoming increasingly popular. The one-piece sinks which may be fabricated of stoneware afford complete insurance against leakage and the permanence of stoneware drains and vent lines recommends their use.

Lubricated Stoneware Valves

One of the constant worries of the plant operator has been the tendency of valves of all kinds to freeze tight in service so that ordinary efforts to free them with hammers and wrenches became dangerous. This has been particularly true of plug valves made of stoneware. The Knight-Merco lubricated plug valve, the principle of which has been used in valves of other materials but which is made in chemical stoneware by Maurice A. Knight, eliminates this danger. The underlying patented principle of this valve is the combination in an ordinary plug cock of lubricating ducts in the plug and a lubricant chamber at its base. The lubricating chamber and ducts are so located that when the lubricant control screw in the top of the plug is screwed down the plug is lifted from its seat in much the same manner as the plunger of a hydraulic press. At the same time that the plug is lifted, lubricant is forced through the ducts to the valve's seating surfaces to be distributed evenly when it is turned. No matter how badly the plug may be frozen, this method will free it easily without danger of breakage.



Knight-Merco Lubricated Plug Cock

Porous Carboy Stoppers

The development of a porous stoneware stopper for carboys is an improvement to the credit of stoneware manufacturers. Carboys have ordinarily been closed by glazed, vitrified, or semivitrified earthenware or glass stoppers, impenetrable to gases or liquids. Frequent breakage in transit or in storage, resulting from the development of pressure within them for one reason or another, causes much needless damage and has now led to the perfection of a porous stoneware stopper through which any generated pressure may vent itself without harm. The stoppers are tough, strong, and acid-proof, yet sufficiently porous to vent any gas that might be generated and at the same time prevent loss of liquid. Proper standards for these stoppers have been set by the Bureau of Explosives.

Pressure Cast Stoneware

To meet the requirements of some users of stoneware, the General Ceramics Company, whose specialty has been rather the design and erection of plants than the manufacture of material on a quantity basis, has developed and is now using a new process for the manufacture of very close grained ware. This process consists of casting the suspension of clay in water—more of a suspension than a plastic mud—in molds under pressure. By this means it is possible to get a very close grained ware, free from air holes, and resembling porcelain in texture. The accuracy of dimension and shape of the finished piece is easily controlled in ware made by this process. After casting, the ware goes through the series of aging, curing, drying, and burning operations as ordinarily practiced.

Special clay bodies are used by this company for special purposes, permitting a wide variation in the properties of the ware and allowing emphasis to be placed upon any desired property, such as plasticity, tensile strength, elasticity, and so on. By so selecting clays it is possible to build tanks of capacities up to some 4500 liters (1200 gallons) capacity in a single piece, pipe joints as long as 4.27 meters (14 feet), and square tanks with a maximum dimension of 3.65 meters (12 feet).

In addition to the special pieces which this firm makes, a new acid-proof white glaze of its development has made possible the manufacture of satisfactory special pots for use by jewelers and others for the evaporation of very corrosive, and at the same time very valuable, solutions. The white glaze makes possible complete recovery of slight traces of solution or valuable sediment and the excellent heat-resistant properties of the ware largely prevent breakage in use. Furthermore, it adds to ease of complete cleaning where sanitation is important. White glaze, which has not before been practicable on chemical stoneware, can now be applied to it wherever desirable.

Glass as a Plant Construction Material

Pyrex glass, developed originally by the Corning Glass Works to meet the need for better lenses in railroad signal systems and later widely used as a laboratory and household glassware, possesses many properties which recommend it as a material for plant construction. Following its early use in condenser tubes for Hart nitric acid equipment, it has been gradually working its way into all parts of plants. Pyrex evaporating dishes up to 61 cm. (24 inches) diameter, drying trays up to 30 cm. × 45 cm. (12 × 18 inches), retorts of 72 liters (19 gallons) capacity, and a wide variety of pots up to 45 liters (12 gallons) capacity are in everyday use in industry.

Glass lends itself readily to tube fabrication by drawing for small sizes and by molding for the larger sizes generally classed as pipe. Pyrex tubes with socket ends find extensive application in acid-pumping lines, thousands of meters being in use in nitric and hydrochloric acid plants. Recently pulsometers (montejus) have been produced of it, thus making available complete pumping systems of this one material. In the larger molded sizes Pyrex pipe is used for tower assemblies, still columns, gas mains, etc., the joints usually being made with a flexible cement resistant to the substances handled. Tubing in small sizes is used to a considerable extent in short lengths as a tower packing.

Tubular evaporators and condensers have also been built with Pyrex as a tube material, and some interesting developments are foreshadowed in this particular field. It does not conduct heat so readily as the majority of metals, but the over-all heat transfer values are sufficiently high for commercial work as the perfection of the glass surfaces and the retention of these under corrosive conditions tend to offset the lower conductivity value.

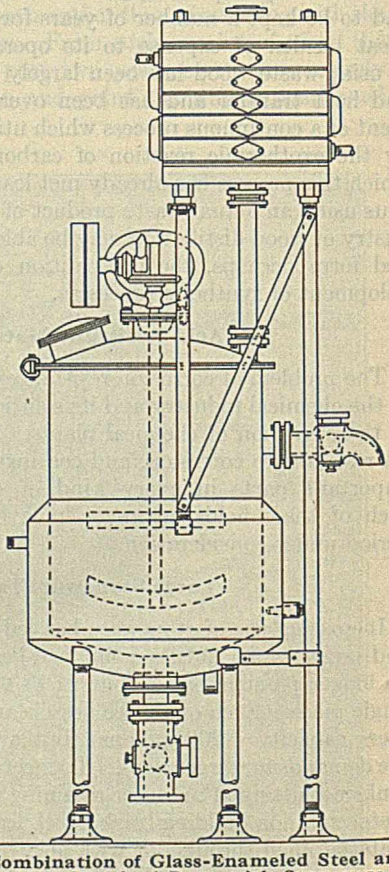
The smooth, hard surface of the glass has led to its use in molded rollers used in artificial silk manufacture, textile dyeing machines, and various coating devices such as stamp gummers. Small one-piece bearings have given excellent service on experimental machines, and it is believed that further development of manufacturing processes will make it a valuable material for this purpose. Its transparency, coupled with its low thermal expansion, has led to wide use for sight glasses for evaporators, reaction kettles, columns, pipe lines, and oil refinery "look-boxes." Its electrical insulating properties are opening up other new fields of use.

Corrosion-Resistant Coatings

The idea of protecting a strong but easily corroded material by a less strong but more resistant one is not new, but its development continues to produce new and better forms of equipment to meet the diversified needs of a growing chemical industry. Glass and various related enamels have been applied to the protection of ferrous metal vessels of various kinds. Plating and more or less definite welding of resistant metals or other materials on others less so offer other types of corrosion-resistant ware. Each kind of ware has definite advantages of its own for particular purposes and all may be used in the same plant for different parts even of the same operation. In each progress has been made during the period under discussion.

Glass-Enameled Ware

Improvements in enamel composition, in methods of fabricating shapes, in the design of furnaces, and in equipment for mechanical handling of ware in process have made possible the production of enameled ware of increasingly better quality and at much lower costs. The application to a steel base of a highly resistant enamel, which had formerly been applied only to cast iron, has made possible much greater flexibility of design and has eliminated to a great extent the necessity of conforming to standard patterns. The welding torch makes feasible the manufacture of great varieties of shapes from steel, including complicated jacketed pieces, and combinations of cast iron and steel, coated with the same resistant enamel, make possible a range of design hitherto impracticable. The recognition of fusion welding as a proper


Combination of Glass-Enameled Steel and Cast Iron Standard Parts with Stoneware in the Same Piece

means for the fabrication of pressure units by the Boiler Code Committee of the A.S.M.E. and the promulgation by it of definite specifications for welded enameled vessels have given a considerable impetus to this use of enameled equipment. Enameled pipe made on a cast-iron base instead of the more expensive welded steel is finding considerable favor, as the cost of the product has thus been considerably reduced without impairing its efficiency. These advances and others in this field have been made by the Pfaudler Company, with which the Elyria Enameled Products Company was combined in 1924.

Mechanical improvements in enameled equipment have kept pace with improvements in the mechanical design of plants generally. Especially important has been the standardization of various units so that quite complex layouts may be realized at much lower costs than are involved in completely new designs. In this way, many of the smaller units whose cost has been prohibitive are now available at attractive figures. Closed storage units, jacketed agitators, and a new type of special emulsifier have thus been standardized, and in addition to these a wide variety of other pieces of standard size and quality are to be had cheaply. Typical installations employing these standard parts are used for separating immiscible liquids, for high-temperature vacuum distillation of sensitive organic compounds, for organic condensations, and for a great variety of other purposes from the solution of noble metals in aqua regia to the manufacture of cold cream. The fact that almost any substance or mixture of substances may be handled in this type of equipment under widely varying conditions of temperature and pressure without contamination makes especially welcome the news that such equipment is available at lower prices.

A Rubber-Protected Pump

A centrifugal pump protected throughout by an integral coating of hard rubber has recently been developed by the Oliver Continuous Filter Company. This pump has all the operating characteristics of an ordinary centrifugal pump but with the added ability to handle corrosive solutions with complete satisfaction. The hard rubber covering for the exposed parts of the pump gives it many advantages over some of the other types in which corrosion resistance cannot be combined with the strength of iron.

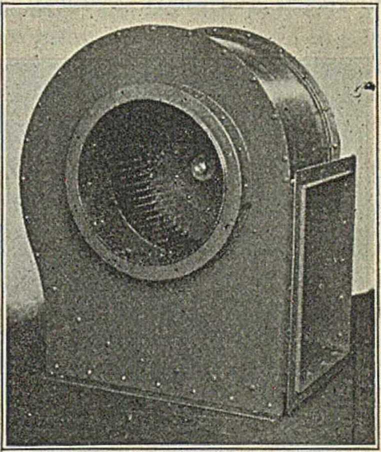
Corrosion-Resistant Metals

To supplement its lines of acid-resistant equipment, more particularly in the field ordinarily covered by machined pieces and those fabricated from sheet, the Duriron Company has developed a new nonferrous alloy, called Alcumite. This alloy may be forged, sheared, punched, and machined as readily as medium carbon steel. It may be welded in the oxy-acetylene flame and is available in the form of castings. It shows remarkable resistance to corrosion by sulfuric, hydrochloric (of low strength), phosphoric, acetic, and sulfurous acids, and by many other corrosive solutions. It is also resistant to the corrosive action of chlorine, sulfur dioxide, ammonia, hydrogen sulfide, and other gases. It is not recommended for handling nitric acid or chlorine solutions. Its melting point is 1040° C. (1900° F.). The following tabulation shows its physical properties:

CONDITION	Brinell hardness	Ultimate tensile strength Lbs./sq. in.	Elongation in 2 inches Per cent
Cast	130	75,000	30
Hot-rolled	195	110,000	10
Hot-rolled, annealed	141	90,000	25

Alcumite is available in hot-rolled annealed sheets from 12 mm. (0.5 inch) to No. 24 U. S. standard gage, and in hot-rolled rods, bolts, nuts, and similar fittings in great variety. Gate valves made of it are giving satisfaction in various industries where it is necessary to handle weak solutions of sulfuric acid and other corrosive liquids. Standard Viking rotary pumps and Sirocco blowers made of this metal are already on the market for use in handling corrosive liquids and gases. These are of standard construction and the efficiency of operation of the usual types is preserved since no change of design has been necessary.

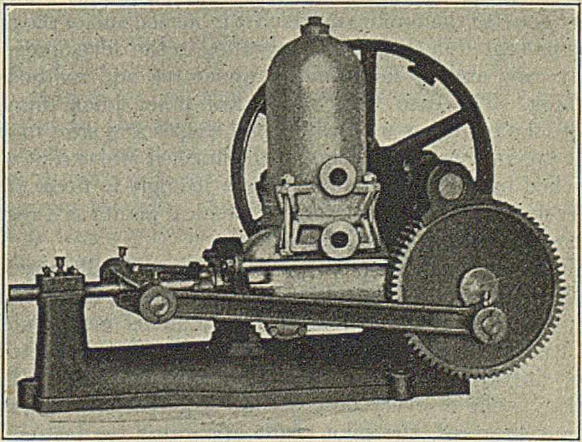
High-silicon iron readily takes a high place among acid-resistant metals, but the difficulties met in its fabrication have made its complete development for chemical uses a slow process in spite of the energy with which this has been undertaken. New pieces are being constantly made and progressive standardization is counteracting the high cost incident to special patterns.



Sirocco Blower Built of Acid-Resistant Alcumite

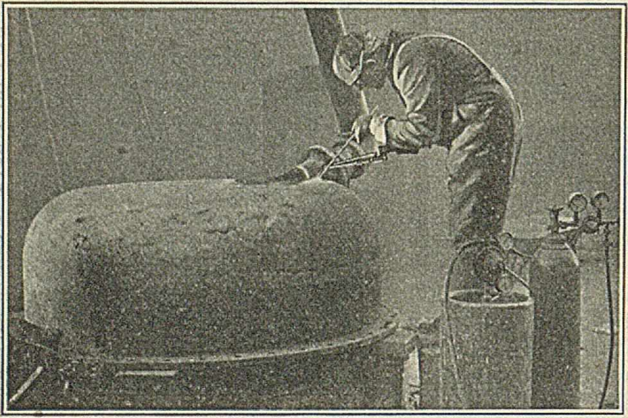
Among the new apparatus in Duriron which have been made and standardized during the recent past are a double-acting reciprocating pump, especially adapted for low capacities against high heads, a larger centrifugal pump than has previously been standard, and a large-capacity ventilating fan for moving corrosive gases against frictional resistance.

The new reciprocating pump is constructed with only three gasket joints, and by a special patented arrangement the stuffing box is kept under slight suction to prevent as far as possible its contact with the corrosive liquid. The four ball valves required may be made of Duriron or such other material as may seem best for the particular use to which it is put. Its efficiency is high, 65 per cent, many times higher than that of a centrifugal pump operated within the range of capacity of the reciprocating unit. This pump is especially adapted for tower operations as it will operate continuously at low capacities against high heads with low power consumption. The larger centrifugal pump unit, similar to already standard designs, is provided with 76-mm. (6-inch) suction and 50-mm. (4-inch) discharge connections. It



Duriron Reciprocating Pump

is equipped, as are the smaller sizes, with a stuffing-box guide bearing, which eliminates impeller whip and thus greatly increases the service of stuffing-box packing. An acid-proof ventilating fan for the delivery of several hundred cubic feet of air per minute against a frictional resistance of 7 inches or so of water has been added to the Duriron line. It is particularly satisfactory for use in connection with nitric acid recovery towers and shows a distinct saving compared with steam jets which have been used heretofore.



Acetylene Welding of Cast Iron Pot

Design of Apparatus

The special conditions to be met in all kinds of chemical manufacturing operations have given this industry a greater variety of equipment made to fit into systems of the utmost complexity and operated under more widely different circumstances than any other. The necessity for meeting exactly the requirements of new processes has made oxy-acetylene cutting and welding tools particularly valuable in this field. The acetylene torch is most useful for minor or major alterations or repairs of equipment already in place and for the fabrication of special forms both for experimental and operating purposes. Careful and continuous study of acetylene and the torches in which it is burned and of the problems presented in their use has resulted in the development of many new and useful forms of apparatus and methods of working. The ease with which leak-proof joints may be made, the readiness with which odd shapes and sizes may be built up, and the permanence of the finished job, except when attacked by the cutting torch, argue strongly in favor of the wider use of acetylene welding in chemical plants as a regular part of the maintenance department.

Almost any metal may be worked into practically any form by the proper use of the acetylene torch. Cast and wrought iron, steel, aluminium, copper, brass, monel metal, nickel, and lead are readily handled by it. Pipe lines, jacketed or bare; intricate heating and cooling coils, jacketed or bare; kettles; stills of every description; and, perhaps more important than all, the pilot plant apparatus for testing out processes on a semicommercial scale—usually drawn from the plant's cast-offs and subject to frequent alterations to meet unexpected conditions—all of these are readily constructed by the acetylene welder to meet the most exacting engineering requirements. Sheet metal can be easily handled, but the possibilities which exist for the welder in an ample stock of various pipe sizes are almost limitless from a chemical plant point of view. No difficulty is offered in the construction of every conceivable pipe fitting from the pipe itself. Such things as T's, Y's, U's, L's, and manifolds, which may be quickly required, are child's play for the good welder.

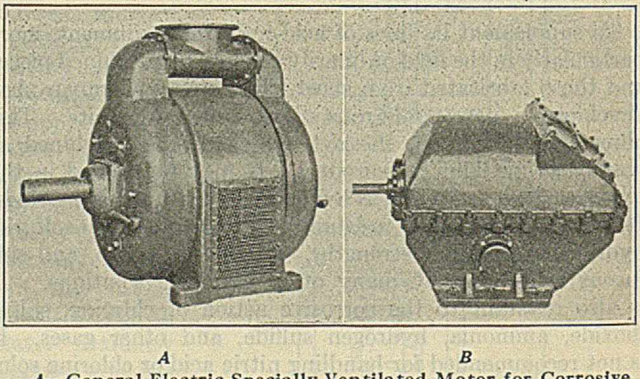
Progress in this field has largely been in the wider introduction of these tools into chemical plants as a result of the assistance rendered through the service engineering staffs of such firms as the Linde Air Products Company, who offer every assistance to the welder in the solution of knotty problems as they arise.

Special Electric Motor Designs

Many of the new developments in the fabrication of chemical equipment have been in the adaptation and improvement of existing forms rather than in the introduction of entirely new forms. Some of the equipment of chemical plants is in the general industrial use, but frequently special adaptations of the usual designs are necessary to meet special conditions. Particularly is this true of power equipment.

As in other industries, the idea of individual motor drive and electrical power transmission is gaining ground in the chemical field. In most cases it is quite safe and economical to use standard motor equipment for individual drives, but in others special precautions are necessary to prevent hazard from explosive or corrosive dust or gases. In dusty locations the difficulty with bearings is largely offset by special construction of the bearing housings, and in some of the more recent standard induction motors the coils are completely incased in a baked-on insulation which gives a smooth, easily cleaned surface highly resistant to various corrosive vapors and abrasive dusts.

In especially corrosive atmospheres a new type of construction, developed by the General Electric Company, consisting of a completely inclosed, self-ventilated induction motor is valuable. Clean air for cooling is piped to the motor, drawn through it by its own fan action, and finally vented from the side without permitting the corrosive atmosphere to gain access to the motor parts. The whole arrangement is very effective in preventing troubles from fumes or vapors which might attack motor windings, slip rings, and so on. Often it is possible to use such a motor or even an ordinary squirrel cage induction motor in flammable atmospheres, but even these types may be dangerous under extreme conditions. To provide the utmost safety in extremely flammable surroundings, this company has developed a motor so completely isolated in its case that it is impossible for an explosion originating within it to be transmitted to even the most dangerous atmosphere. This motor is built in all the popular ratings for both a. c. and d. c. operation and is inclosed in a strong case with wide machine fitted joints. The design is such as to permit necessary cooling through the metal case without requiring ventilation. Severe and exhaustive tests have proved the safety of this construction.



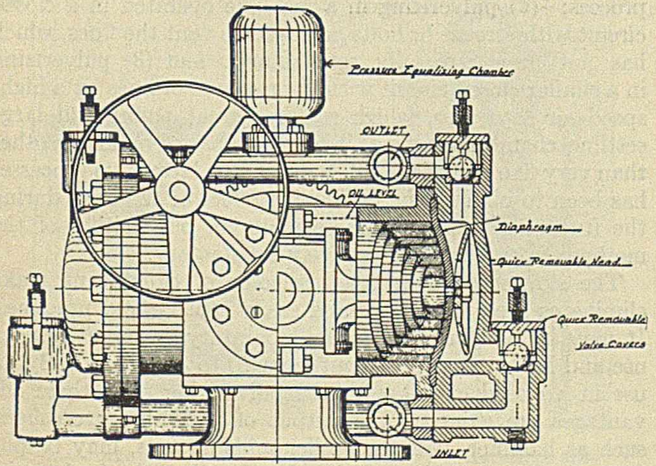
A B

A—General Electric Specially Ventilated Motor for Corrosive Atmospheres. *B*—General Electric Nonventilated Motor for Flammable Atmospheres

A new design of single-phase, variable-speed repulsion motor for direct connection to slow-speed exhaust fans has recently been put on the market by the same firm. For pumps and fans which must frequently be run at reduced speeds an alternating current, "brush shifting," adjustable varying speed motor has been developed having shunt speed characteristics and high efficiency at all speeds. Advances have also been made in the adaptation of motor control devices for use in corrosive and explosive atmospheres. Treatment of the cases makes possible longer life under corrosive conditions and oil immersion of the current-carrying parts and contacts effectively prevents sparking.

Pressure Diaphragm Pumps

The pumping of thick sludges, resulting from the operation of thickeners, into filter presses for final dewatering has always offered difficulty to the user as well as the designer of such equipment. Recently T. Shriver & Company has developed a diaphragm pump for producing pressures up to 150 pounds per square inch which can be built to resist corrosive agents and which gives entire satisfaction in handling such materials. The pump is of the double-acting type and all moving parts are separated from the liquid to be pumped by rubber diaphragms. These are supported at all points by a series of concentric cylinders operating in a bath of lubricant, which transmit power to them from an eccentric. The liquid ends of the pump consist of two pairs of simple, easily replaced castings, which can be made of any of the usual corrosion-resistant alloys. The valves used are of the self-cleaning ball type and are easily replaceable. The efficiency of this pump is unusually high because the moving parts operate entirely in a bath of oil and for the same reason its life is much longer than that of ordinary pumps used for similar purposes. It is the first pump of the diaphragm type capable of developing pressures sufficient for filter press operation, although its use is by no means confined to this field. It is finding wide use in pumping corrosive liquids and especially those containing abrasive sediments. Heavy muds of every description are readily handled by it.



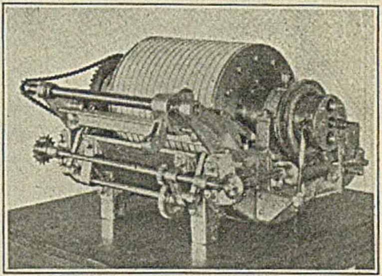
Shriver Pressure Diaphragm Pump

The difficulty of pumping thick sludges for considerable distances or against low pressures has been met by the development of a similar double-acting diaphragm force pump by the Dorr Company. This pump consists of two rubber diaphragms mounted on an eccentric with a water seal between them. It is designed to supplement the regular Dorrco suction pump and is recommended to work against heads as great as 40 feet of water in handling thick sludges. The standard Dorrco diaphragm suction pump has also been improved by the replacement of its flat valves by ball valves, which give more positive action when there are pieces of foreign matter present which might hold the older type open.

Filtration

New developments in filters have been principally in the field of new applications, according to the United Filters Corporation. Their disk type, continuous rotary filter is finding new uses in recovering fiber from the white water of paper and pulp mills and in dewatering concentrates from flotation machines in the mining industries, wet process slurries before they go to the kilns in cement manufacture, clay slurries in the ceramic industry, and the dust recovered by washing from blast furnace gases. The refining and bleaching of all kinds of petroleum products and the separation of petrolatum and amorphous waxes from oil stocks are fields in the petroleum industry where pressure leaf type filters are finding wide and successful use.

Oliver continuous filters are similarly finding new uses. The dewatering of activated sewage sludge and the recovery of fiber from the white water of paper mills are among the outstanding developments of the last two years. A specially constructed Oliver filter is being favorably received by the ammonia process soda manufacturers in handling sodium bicarbonate on a large scale.



Oliver Laboratory Model Continuous Filter

In addition to the development of its regular commercial filters, this firm has also standardized a laboratory model which is an exact replica of the larger machines and which is especially designed for use in schools of chemical engineering. This miniature filter duplicates exactly the operating characteristics of its prototype but has an effective filtering area of only 3 square feet and can be readily installed in a space 3 feet square. It is made of both cast iron and acid-resisting bronze.

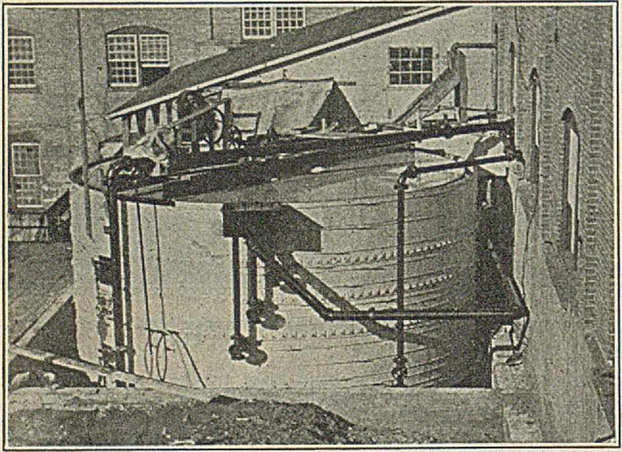
Thickening and Clarification

A new clarifier-thickener, combining the usual gravity sedimentation with filtration, has been developed by the Hardinge Company. It consists essentially of a filter similar to a sand filter, although other materials may be used, mounted in the bottom of a regular gravity decantation thickener. The suspension to be separated is fed in and allowed to settle out its solids on the filter bed while the clear liquid goes through. As the solids accumulate on the filter medium they are scraped into a thickened paste outlet in the center of the tank bottom by a spiral scraper. This scraper removes a small layer of the filter medium (a fraction of an inch) with each revolution and hence keeps the filter bed clean and active. The advantages of this machine over the ordinary type of continuous decanter are in the greater capacity, greater concentration of the thickened pulp and greater clarity of filtrate made possible by the combined action of the filter and gravity. It operates continuously on a very low power consumption. The pulp that it will turn out continuously depends largely on the material of which it is composed, but exhaustive tests have shown this to be more concentrated than that turned out by other similar devices. It is particularly adapted for use as a clarifier where a clear filtrate is essential.

Continuous Countercurrent Decantation

In this field the developments of the Dorr Company must command the respect of all. Their well-known thickeners, agitators, and classifiers have gone through regular steps of improvement and have been found useful in an increasing number of industries.

The Dorr agitator has been improved by building it of acid-resistant materials, and very recently an agitator has been built with submerged parts of Duriron keyed together with Duriron keys instead of bolted as is customary. This construction permits easy replacement of worn or damaged parts. A further development of the agitator is a modification particularly suited for use in mixing cement slurry. Another modification is built on a solid shaft with part of the air for agitation emitted part way down the shaft and the rest inside a cylindrical collar near its bottom. In some cases it is objectionable to use air for agitation and to obviate this difficulty an impeller type agitator has been developed. This consists essentially of the standard machine in which the agitating arms have been replaced by rakes and which is provided with a propellor operating in a draft tube in the center.



Dorr Save-All Thickener Operating on White Water from Paper Mill

The Dorr washing thickener is an important new development of this well-known apparatus. It consists of a series of trays which operate in series instead of in parallel as in the ordinary tray thickener. It is thus possible to do the work of several countercurrent thickeners in the space that would be ordinarily occupied by one. In reality it consists of several machines mounted one above another. The ordinary tray type thickener has also been improved making each compartment or tray do its part of the work by dividing the feeds. This last type is finding particularly economical use in the recovery of fiber from the white water of paper and pulp plants. It is desirable at times to use every available bit of floor space for clarifying operations and to meet this situation a clarifier and thickener has been designed in which the tanks used are square. Special rakes have been devised to sweep the entire bottoms of the tanks.

In the application of the continuous countercurrent decantation as secured by this type of machinery, early use in causticizing with lime and in the mining industries has been supplemented by several new applications and by wider use in old fields. The recovery of values from industrial wastes and the purification of municipal sewage have long shown economies effected by such equipment. Large savings in fuel, material, and labor have been effected by the introduction of Dorr machines for the clarifications of sugar juices prior to evaporation, as in the Petree-Dorr process.[1] In chemical manufacture, aluminium sulfate, barium sulfide, phosphoric acid, superphosphates, and phosphate salts are made more economically by the use of this principle. The Dorr Multideck classifier is finding wide use in the washing of crystals, especially the crystals of salt which are common in the underflow from electrolytic caustic soda evaporators.

The latest development in the use of this type of equipment has resulted, like the increasing use of save-alls in the paper industry, from legal restrictions, placed this time upon iron blast furnaces. It is now necessary to recover from the flue gases the fine dust formerly thrown into the streams, and return it to the furnace. This is easily and economically accomplished by the use of a gas water washer to separate the dust from the flue gases, a Dorr thickener, and finally a continuous rotary filter to dewater the sludge before its return to the furnace. Such installations have been called upon to handle more than 100 tons of dust daily and this has been accomplished at a cost which permits the recovered iron to yield a profit on the operation.

Grinding and Pulverizing

A modification of the well-known Hardinge continuous conical mill has recently been put on the market for batch grinding on the same principle. This batch mill is particularly adapted to the fine grinding of inks, paints, and enamels, and offers considerable advantages over the older cylindrical ball mills which have been used for this purpose. The grinding action of balls or pebbles thrown together toward the larger diameter in the middle by the action of the conical ends of the mill is utilized in this as in the continuous mill. This batch mill possesses several advantages over the usual type of cylindrical mill in savings of floor space, reduction in the wear and tear on lining, and in a considerable reduction in the time required to discharge its contents.

Slow-Speed Centrifugal Air Separators

Three methods of fine grinding have been in use: (1) pulverizing in a machine which discharges its entire product of the desired fineness, usually a slow and uneconomical process; (2) pulverizing in a machine operated in a closed circuit with screens or bolts arranged to vent the fines, which has not been especially satisfactory; and (3) pulverizing in a similar closed circuit with the removal of fines by a high-speed air separator, which requires great power and large settling chambers and which is incapable of handling other than very fine materials. The aim in the latter two processes has been to obviate the cushioning effect of the fines during the further grinding of coarse material, but neither of the methods in use has been entirely satisfactory.

The slow-speed centrifugal selector of Sturtevant make eliminates these objections and easily replaces old practices. It may be had in all sizes for laboratory to large tonnage use and has a range of output from 40 to 350 mesh. By its use in a closed circuit with the pulverizing unit, these advantages are gained: the output of preliminary crushers, such as hammer, ball, and roller mills or rolls, may be put through the selector to remove fines so that the feed to the finishing pulverizer contains a negligible amount of material which it is unnecessary to regrind; the finishing mill may be adjusted to operate at a higher rate, finishing only part of its output and depending entirely upon the separator to regulate fineness and return clean oversizes for further grinding; and these improvements in the cycle result in greatly increased capacity with lower power requirement and less attention, at the same time giving certainty of uniform output. With roller or ball mills the ordinary screens may be much coarser or may even be removed entirely. Even the old millstones may be used economically for many grinding operations, if they are supplemented by this type of separator, as it obviates entirely the necessity of "pinching"

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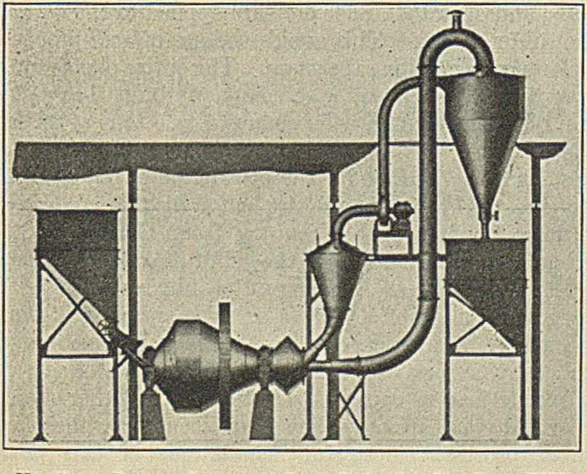
[1] Hartmann, This Journal, 16, 1178 (1924).

the stones to secure the desired fineness. The removal of extremely fine material from the output of a mill by means of screens becomes uneconomical beyond a certain fineness and so it is often practice to use such an air separator to supplement screens for the removal of "floats."

In order to increase the capacity of its conical mills and at the same time assure proper uniformity of its product, the Hardinge Company has developed two new rotary classifiers operating on the principle of reversed air currents and specifically for use with its own mills. The rotary classifier is designed to give a product from 98 per cent passing a 48 mesh to 80 per cent passing 200 mesh. Where greater fineness is required, the rotary and superfine classifier is used. The equipment is very simple, all auxiliary apparatus having been eliminated. The same volume of air is used throughout the entire process, separation being effected by regulation of velocity in various parts of the classifier. The current first enters the mill, stirs up the material, and hastens discharge of fines. As the material enters the classifier, the same current carries the fines directly to the finished product bin, and, returning at a greater velocity, blows the oversizes back to the grinding zone, where the same operation begins over again. This prompt removal of fines greatly increases the capacity of the mill, and hence its efficiency, because its grinding action is not expended on material already of the required fineness. The air circulation is secured by a fan in the circuit. These classifiers can be had in capacities ranging from 180 kg. (400 pounds) to 43 metric tons (35 tons) per hour for the rotary and from 135 kg. (300 pounds) to 28 metric tons (23 tons) per hour for the superfine rotary. The differences between the two types are only such as are made necessary by the difference in fineness of output. They are finding extensive use in connection with the Hardinge mill for grinding and classifying ceramic materials, limestone, shale, coal, and so on.

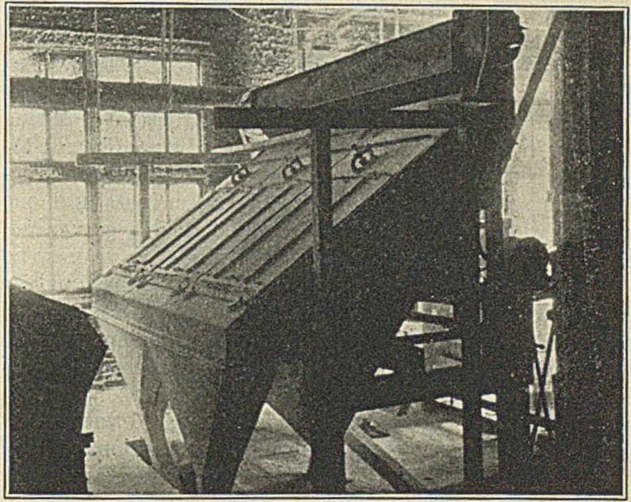


Hardinge Rotary Separator Installed with Hardinge Mill

Mechanical Separation

Patent Office records show an unusual number of inventions of screening devices since the first development of the inclined vibrating type, which has shown such radical improvement over the older revolving, bumping, and gravity mechanisms of a decade ago. The superiority of the inclined vibrating type has led many to devise modifications and improvements, but few of these have been successful.

Screening to the uninitiated seems an easy proposition, for by simply placing a screen at an angle of 45 degrees and whipping its surface with a small stick even the most difficult material may be made to pass through fine meshes. Thus far the problem and its solution are simple. But the design of a machine which will operate mechanically 10 to 24 hours per day without undue wear of the vibrating mechanism or of the delicate screen clothing, and which will at the same time produce large tonnages without blinding, is far from simple. The discard of inefficient screens will show a hundred failures to one success. However, the successes have clearly shown the principle to be practicable and so great an advance over former methods as to assure permanency. The Sturtevant Mill Company has been a leader in this development.



Typical Installation of Sturtevant Vibrating Screen

Vibration is necessary which will keep the material active and yet not cause the particles to jump too far, skipping over the screen surface without proper opportunity to pass through the meshes, and which at the same time is evenly distributed over the wire to prevent blinding and is destructive neither to clothing nor mechanism. Unit construction and accessibility, which allow quick repairs and the interchange of screen frames, with no parts too heavy and cumbersome to be handled easily, and a feeding device which spreads the material evenly over the entire clothing, are noteworthy features of latest and most successful screens.

Spray Drying

Spray drying is becoming increasingly popular for handling materials of a delicate nature which must be completely dried. The Krause disk spray process, controlled by the Chemical Construction Company, offers many advantages for this operation. It consists primarily of a chamber in the middle of which is a horizontal steel disk revolved at very high speeds (5000 to 24,000 r. p. m.) on to which the solution to be dried is dropped from above. At the high speed of revolution of the disk, the liquid—which may or may not be put through a preliminary partial evaporation—is thrown violently in a very fine spray into a stream of hot air entering from below. The liquid is completely evaporated, leaving the solid matter in a fine state of subdivision to be collected in a dust-collecting system. The advantage of this process is in the fineness of dispersion of the liquid being dried and hence the rapidity of drying and the short length of time that the finished material is in contact with the hot air. The product of such an operation is unchanged from the form in which it existed in the solution except for the complete and almost instantaneous removal of the liquid phase.

Air Conditioning and Drying

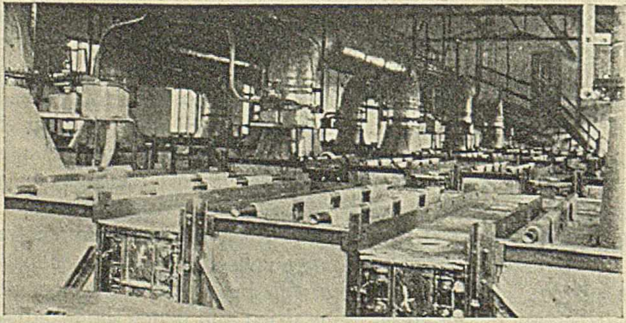
The well-known principle of Carrier air-conditioning equipment has been recently applied to driers. This follows the use of automatic temperature and humidity controls with the air-conditioning apparatus which have made possible its completely automatic operation throughout any desired cycle. The drier is so constructed that the air, brought to any desired temperature and humidity, enters the drying chamber through a series of nozzles near the ceiling and passes toward the opposite end of the chamber over the material arranged on trays but not impinging upon it. In this way a positive pressure is built up at the opposite end of the chamber which forces the air back through the trays to the entrance end in the bottom of which is located the outlet. The ejector action of the nozzles causes a constant circulation of air in the chamber equivalent to three to five times that which the supply fan alone would cause.

A recent innovation has been the construction of drying chambers in standard sections which may be readily put together to get any desired size of chamber. These construction units are available in four standard heights and one standard width. The units are built of double galvanized iron with air cell asbestos or magnesia insulation as may be required and are more efficient than 150-mm. (6-inch) hollow tile plastered inside and out. The ease with which a drier may be built from such units and moved from place to place when necessary, the efficiency of insulation, the lightness of the construction, the advantages of the fireproof feature, and the low cost per unit of area as compared with other equally satisfactory types recommend these sectional driers. They are obtainable with or without ejector units and automatic controls.

A laboratory edition of the Carrier ejector drier for duplicating large-scale operations for test has also been put on the market. It is equipped with an ejector circulating system, electric heating elements, a spray device for controlling humidity, and any desired combination of automatic controls. A further provision is made for drying samples directly on a balance pan, making it possible to follow accurately the progress of the operation.

Sulfuric Acid Manufacture

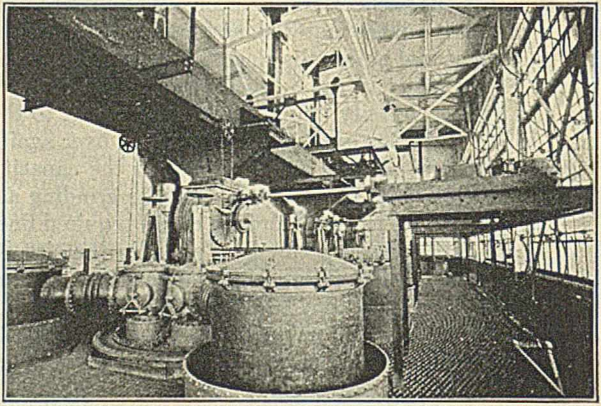
Even the "pig iron" of the chemical industry, sulfuric acid, has come in for its share of improvement during the past two years. The Chemical Construction Company is responsible for the development of a new sulfur burner, a new small-scale process for the manufacture of sulfuric acid, and the introduction from abroad of the Schmiedel process developed there.



Reaction Chambers in Schmiedel Sulfuric Acid Plant

The principle of the Chemico sulfur burner is similar to that of a spray oil burner. The sulfur is melted and fed to a spray nozzle to be burned in spray form. This burner is practically automatic in its action, and is completely flexible in operation. Its principal advantages are that it requires less space than any other burner now on the market, burning is complete, and there is no tendency for the formation of sulfur trioxide. It is useful in sulfuric acid manufacture and especially in the manufacture of sulfite liquor in the paper industry.

Small-scale sulfuric acid manufacture has always been difficult and uneconomical, but the patented pressure process recently developed seems to offer a satisfactory solution of this problem for the user of comparatively small quantities of acid in noncompetitive localities. In this process, which is practicable in units turning out as little as 4 tons of 60° Bé. acid per day, the sulfur dioxide from the burner is introduced under pressure into a sealed tower which replaces the ordinary chamber system. As it goes in, the sulfur dioxide is passed under an acid seal, from which it liberates the necessary nitrous gases. The reaction is then completed in a series of secondary reaction chambers as the mixed gases pass up the tower. The oxides of nitrogen liberated in the reaction are re-absorbed in the usual form of Gay-Lussac tower. A special feature of this type of plant is that the entire system is sealed and operated under pressure applied to the air going to the sulfur burner. This avoids the use of acid-proof fans and blowers for handling the gases. The entire plant requires little expert attention and is so compactly built that a single 47-cm. (18-inch) column will produce 4 to 5 tons of 60° acid per day.



Retorts in Badger-Stafford Wood Distillation Plant

The Schmiedel process for the production of 60° acid from waste gases of low or fluctuating sulfur dioxide content has been introduced into this country from Germany. It is based on a method of bringing the sulfur dioxide into contact with the largest possible amount of nitrosyl acid in the finest possible state of subdivision. The spraying of the nitrosyl acid is accomplished in a specially designed mixing chamber by a series of acid-proof rollers rotated at very high speeds just in contact with the acid. Otherwise, the process and plant are only slightly different from the regular chamber process. Successful installations of this process have been in operation in Germany for several years and one is now operating in this country.

Hydrochloric Acid

An improved furnace for the manufacture of hydrochloric acid and salt cake, the Bäyer furnace, has been in operation in Germany for a number of years and has now been brought to the United States by the Chemical Construction Company. This furnace utilizes 90 to 98 per cent sulfuric acid—although 60° acid may be used with no other harm than a corresponding reduction of output—and any good grade of salt. It is economical of labor and of power and turns out salt cake ready for use. A plant turning out 45 to 52 tons of salt cake and 75 to 88 tons of 30 per cent acid per day can be operated by thirty men with a power consumption of about 3 kilowatts.

Wood Distillation

In the field of destructive distillation a process and necessary equipment for the economical retorting of finely divided wood, sawdust, chips, and other similar waste cellulose materials has long been sought with little success until the work of O. F. Stafford, of the University of Oregon, developed a process which has recently been put into operation by E. B. Badger & Sons Company. The first commercial installation of this process was made about two years ago and upon the success of this the Ford Motor Company decided upon a plant using it for the recovery of by-products from its waste. This large plant is now in operation at Iron Mountain, Mich. The process makes use of the heat liberated by the exothermic decomposition of cellulose at carbonizing temperatures and hence obviates the difficulties of heat transfer from sources outside the retort. By predrying and preheating the finely divided wood and by introducing it into the retort with material already undergoing carbonization, the heat generated by the decomposition is sufficient to keep the reaction going continuously. It avoids the necessity for complex agitating devices to insure complete carbonization and obviates the loss of heat which is inherent in its introduction through so good an insulator as wood chips. To make the process successful on a large scale it has been necessary to develop special driers for chips, special coolers for handling the finely divided charcoal as produced, and special briquetting machines to make this into a commercial product.

Evaporators

Among the other developments of the Badger Company is a horizontal film evaporator which is particularly adapted for handling comparatively small amounts of sensitive or corrosive materials. The apparatus is automatic and continuous in operation and occupies small space. It is particularly successful in replacing open pan evaporators handling such solutions as those of zinc chloride, sodium perchlorate, ammonium chloride, sodium acetate, sodium sulfate, and glue.

Glass Evaporator Tubes

In discussing the industrial uses of Pyrex glass, mention was made of an evaporator in which this glass is used as the tube material. The evaporator is of the Yaryan type built by the Swenson Evaporator Company and is particularly adapted for use with very corrosive liquids, such as nitric acid, ferric chloride, or for very delicate solutions, such as fruit juices, which are injured by contact with metal during evaporation. It operates on the film evaporation principle so that heating of the liquid is reduced to a minimum—contact of the liquid with the heating surface is ordinarily less than a minute. The vapor headers, vapor piping, catch-alls, and thick liquor receivers are built of chemical stoneware so that the entire construction is acid-proof. No case of breakage of the glass tubes has yet been noted in these evaporators during regular operation, which speaks well for its excellence for this purpose.

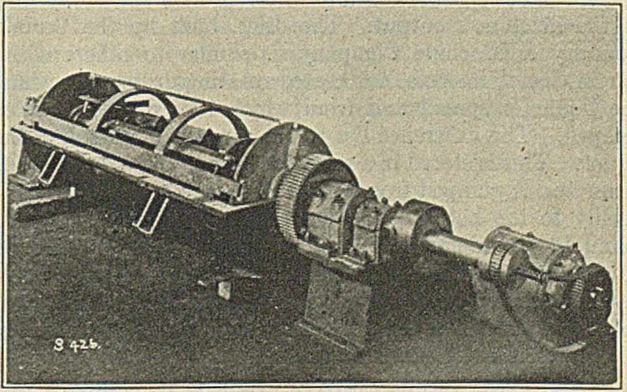
Continued improvement has been made in the construction of the Swenson-Yaryan evaporator. Most of these changes have been mechanical and include a swinging cover plate over the return bends, which greatly facilitates cleaning of tubes; a new design of catch-all, requiring less space and giving greater efficiency; and a special expansion joint combined with the ordinary joint between the main body and the vapor head, which eliminates the problem of the leaking of tubes when rolled into the tube sheets, whether the expansion comes in the tubes or shell.

Evaporation of Difficult Solutions

For the evaporation of solutions of substances which have inverted solubility characteristics, such as anhydrous sodium sulfate and sodium carbonate monohydrate, ordinary evaporators lose their efficiency on account of the building up of crystal layers on the heating surfaces, and thus materially reducing heat flow. To offset this difficulty, the Swenson Company has devised and patented an external circulating and liquor superheating system, which greatly increases the efficiency of its vertical tube, basket type evaporator and makes it satisfactory for this use. The system consists of continuously withdrawing a small portion of the liquor from the evaporator, pumping this through an external heater, and returning it again through distributing nozzles located beneath the steam basket in the body of the evaporator. This liquor, which is at a much higher temperature than that in the evaporator, causes a violent flashing up of steam. This delays salting out on the heating surfaces sufficiently to permit commercially economical operation by increasing circulation with little power expenditure, by distributing seed crystals through the liquor—which promotes crystal formation as opposed to salting out—and by the scouring action of these growing crystals as they are violently driven through the tubes. The use of this system increases the capacity of evaporators working on such solutions to about 300 per cent of that attained without it, and it further permits the use of multiple-effect installations on these extremely troublesome salts.

Continuous Crystallizer

Mechanical improvements have greatly increased the efficiency of the Swenson-Walker continuous crystallizer during the past two years. The crystallizer involves a series of jacketed troughs provided with agitators and arranged in cascade. The crystals and mother liquor overflow from one unit to the next and cooling water is run through the jackets countercurrent to this. The units have been standardized in 3-meter lengths (10 feet) and the cooling jackets have been provided with efficient baffles to assure efficient heat transfer. The system offers many advantages over the vat system, especially in low cost of operation, high uniformity of crystal product, and operation independent of weather conditions. Installations are handling a wide variety of crystallizations with complete satisfaction, including sodium phosphates, sulfate (hydrated), nitrate and carbonate (hydrated), Epsom salt, and copperas.



Swenson-Kipper Drier Showing Construction

To complement the operation of this crystallizer, a dewatering device has been perfected by the same company for separating the crystals from the mother liquor and delivering them to the centrifuge or storage bin. It is particularly recommended for use with crystals that readily fall out of suspension. In use it is bolted directly to the overflow end of the crystallizer.

A Direct or Indirect Heat Drier

A drier to replace the rotary type for some operations—it can also be used for carrying out reactions between solid or semisolid materials—has recently been put on the market under the name Swenson Kipper drier. It is essentially a stationary, horizontal, cylindrical shell containing relatively high speed beater blades for securing intimate contact between solids or solids and gases. The mechanical difficulty caused by the caking of the mass by the high-speed beaters has been overcome by providing a supplementary set of slow-speed scrapers operating between the beaters and the shell. These scrapers are carried on sleeves over the main central shaft on independent bearings and are driven through a standard gear reduction. As a drier, this arrangement is more economical than the rotary type, a unit 2.44 meters (8 feet) long by 51 cm. (20 inches) diameter having the same capacity as a rotary unit 12.2 meters (40 feet) long by 152 cm. (60 inches) diameter. The unit may be arranged for either direct or indirect heating. It is in satisfactory use in the drying of anhydrous sodium sulfate and copperas, the dry neutralization of niter cake by soda ash to produce salt cake, the reduction of sodium sulfate to sulfide, and the roasting of copperas to oxide.

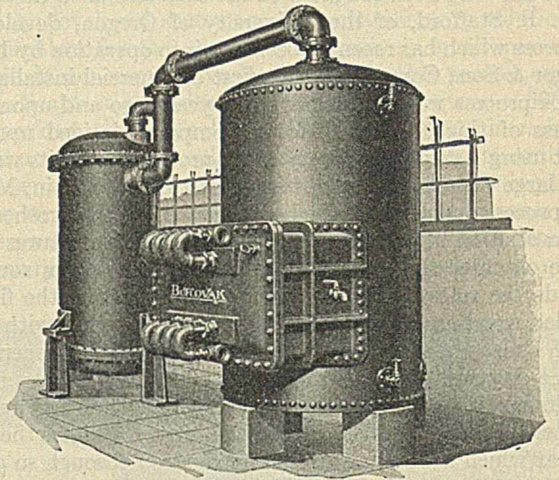
Atmospheric Drum Driers

Drum driers, consisting of heated rotating drums on which the solution to be dried is picked up and from which the solid matter is scraped after drying, either with or without vacuum, have been in use for some time and have proved satisfactory for many kinds of drying operations. More recently there has been developed a similar drier which operates at atmospheric pressure and which is particularly adapted to the drying of solutions containing sediment which might separate out and interfere with the uniformity of the machine's output. The drier, built by the Buffalo Foundry & Machine Company, is similar to others of its line in that it consists of a heated rotating drum onto which the liquor is spread and from which the solid product is scraped. The difference lies in the means for spreading the liquor. This is stored in a reservoir immediately beneath the drum and is pumped from this to a manifold, which feeds it evenly to the hot drum. The spreading system from this manifold is unique in providing that the liquor shall be flowing downward at all points in it to prevent sedimentation in the pipes and outlets of any solid matter which might tend to clog them. The drier operates at atmospheric pressure with free outlet of steam to the air.

This company has also altered details of its standard vacuum drum drier to make it easier to clean, a factor of considerable importance where it is used on food products or others which require maximum cleanliness. In carrying the same idea of sanitation further a steam pump for handling liquor in the drier system has been designed which may be taken completely apart for cleaning by loosening only eight nuts. This feature makes possible the complete cleansing of the pump in minimum time with minimum labor and permits the utmost sanitation.

Industrial Distilled Water

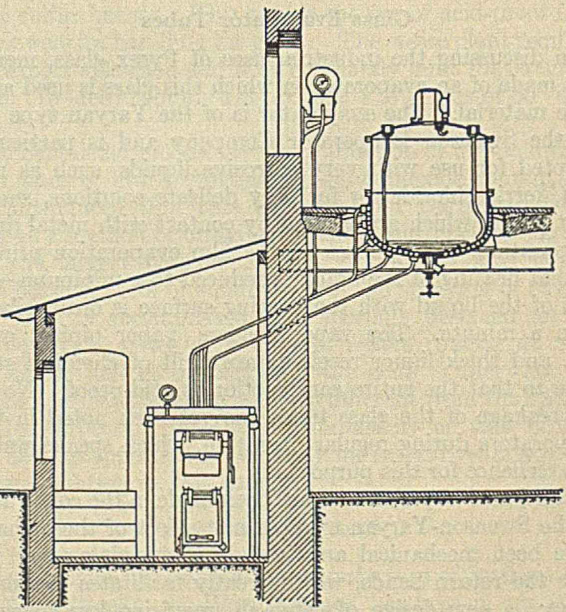
The increasing use of distilled water in industry has led the Buffalo Foundry & Machine Company to design and standardize commercial units for producing it in quantities from 38 to 7570 liters (10 to 2000 gallons) per hour. These stills are built to insure maximum purity of product and may be operated singly or compounded as high as quadruple effect. The distilled water cannot be contaminated by oily steam escaping from leaky joints, as all connections are located outside the evaporator. Ground joints are used throughout, and the cast-bronze steam headers and return bends located outside permit complete accessibility. The heating coils are self-scaling, insuring maximum efficiency of heat transfer.



Single-Effect Distilled Water Evaporator

Heat Transfer

In the field of heated reaction equipment the original Frederking apparatus is a distinct improvement over jacketed vessels. This form of equipment, used in Europe for many years and recently introduced into this country by the Bethlehem Foundry & Machine Company, consists of cast iron with seamless steel tubing cast in it for carrying the heating or cooling medium. The advantages of this construction are the added strength of the coils, embedded as they are in cast iron, the freedom from the possibility of leaks provided by the integral casting of the whole piece, and the efficiency of heat transfer of the intimate metal to metal contact. A further advantage is realized by providing a number of coil inlets and outlets, reducing still further the danger of hot spots, and, coupled with the integral casting of the unit, equalizing temperature throughout. Discharge of residues is greatly simplified in this equipment as compared with direct-fired stills.



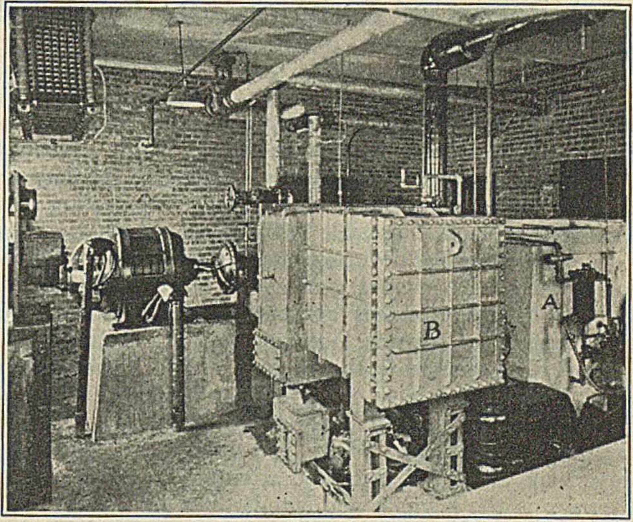
Bethlehem-Frederking Installation

In connection with the Frederking apparatus, the Bethlehem company has developed a hot-water heating system for use up to 350° C., which offers many advantages in accuracy of temperature control and is particularly advantageous for operations where fire hazards must be minimized by locating heating plants at a distance from the still house.

Low-Pressure Refrigeration

In connection with air-processing problems the need of a simple, efficient, foolproof refrigeration system has been felt, and the Carrier company has developed a "centrifugal refrigeration system" to meet this requirement. The use to which this unit is put is principally in supplying cold water or brine to the spray nozzles used to produce cold air of very low humidity.

The system consists of an evaporator, in which the temperature of brine is reduced by the evaporation of the liquid refrigerant, a centrifugal compressor, which is a simple multistage fan similar in type to rotary compressors and steam turbines for creating the vacuum necessary to evaporate the refrigerant, and a condenser, in which the compressed refrigerant is cooled after it leaves the compressor and before the expansion. The entire system is operated under vacuum, the absolute pressure in the evaporator being one pound or less per square inch and that in the condenser, 4 or 5 pounds. This vacuum is maintained by a small auxiliary pump operated at intervals between the evaporator unit and an independent reservoir. The evaporator and condenser units are built of brass for the higher rate of heat transfer which this gives. The refrigerant used is dieline (dichloroethylene). In the evaporator it is expanded around brass tubes containing the brine, and it is similarly cooled by passing over another set of tubes containing the cooling water. The unique features of this system are that the entire operation takes place under pressures below atmospheric, preventing leaks to the outside, that the compressor has no valves, its only contact points are the main bearings, that the drive may be operated at constant speed under a wide variety of load conditions, and that the unit is unusually compact, occupying about a fourth less space than other systems of similar capacity. It is in operation in several industrial plants and is proving itself valuable for use in conjunction with cooling systems for theaters and other public buildings. It is particularly recommended for marine refrigeration, where its safety features as well as the savings in weight and space are important.



Typical Installation of Carrier Centrifugal Refrigeration
A—Evaporator; *B*—Condenser

Conclusion

Such a survey as this cannot be complete, for there is always much work in progress that cannot be discussed because of its intimate relation to the policies of companies for whom it is being done. All members of the Chemical Equipment Association are not represented and much has been accomplished by those in the field who do not belong to this association. This review is sufficient, however, to show the active ingenuity which is responsible for the things here described. It is upon this that the future of American chemistry rests secure.

National Directory of Commodity Specifications

The National Directory of Commodity Specifications, prepared by the Bureau of Standards with the coöperation of the Bureau of Foreign and Domestic Commerce, is now ready for distribution.

This directory contains in convenient form information regarding the best-known specifications for more than 6000 commodities. The book tells not only what specifications are in general use but also by whom they were prepared and where copies may be obtained. In it are conveniently indexed about 27,000 specifications prepared by the Federal Specifications Board and the separate departments of the Federal Government, by state and city purchasing agents, public utilities, technical societies, and trade associations.

The contents include: a statement and endorsement by the Advisory Board; a foreword by Secretary Hoover; a thoroughly classified list of specifications for all types of commodities. There are also included an alphabetical list of commodities, which serves as an index to the specifications, and directions for obtaining copies of specifications listed in the directory.

Official representatives of fourteen leading national societies interested in specifications served as members of a board organized by Secretary Hoover to act in an advisory capacity in connection with the preparation and publication of the directory. In accordance with the recommendations of the advisory board the decimal system of classification was used, the specifications being classified according to "source" rather than the "use" of the commodities. The book is printed on "standard catalog" size sheets in the dictionary or reference-book style, in small but legible type, and thus the number of pages has been kept at the minimum, 385.

Summary of Commodities and Specifications Therefor

Decimal class.	COMMODITY GROUPS	Commodities indexed	Approx. number of specifications
000	Animal and animal products	350	1600
100	Vegetable food products, oil, seeds, expressed oil, and beverages	525	2100
200	Other vegetable products (except fibers and wood)	400	800
300	Textiles	275	1900
400	Wood and paper	625	3300
500	Nonmetallic minerals	725	3300
600	Ores, metals, and manufactures (except machinery and vehicles)	1700	6400
700	Machinery and vehicles	800	2900
800	Chemicals and allied products	600	2400
900	Miscellaneous	650	2400
	TOTAL	6650	27100

The cost of printing and binding the book to the Government Printing Office is only $1.25. The price to the purchaser is the same. Copies may be obtained from the Superintendent of Documents, Government Printing Office, Washington, D. C., by sending with the order, a remittance either in the form of Post Office money order, coupons (issued for the specific purpose of purchasing government publications), express money order, New York draft, or cash—at the sender's own risk. It is important to follow these directions to avoid delay and confusion.

Recent Additions to Tools for Research

A Report of Developments by the Members of the Association of Scientific Apparatus Makers of the U. S. A.

OBSERVATION is the foundation and fabric of research, whose plan is thought. Before profound theories can lead the research worker to the deep secrets of Nature, observation must confirm observation with a minute exactness impossible to the unaided human senses. No amount of logical deduction can replace careful observation of facts. No mental gymnastics, however clever, can do more than supplement our poor human abilities. We must depend for essential accuracy upon those who build our scientific instruments, the magnifiers of the human senses.

It is well that we pause occasionally to determine how well these unsung servants of research are doing their share in advancing civilization. Many new things and many improvements of old will command attention in such a survey. Accuracy is the keynote and standardization the theme of this small but important industry. Its constant labor has been to provide means for accurate observation which will be available to great armies of workers rather than merely to the few who have great resources at their command. Thus we find it following closely the "pioneers at the very borderland of the unknown," duplicating for the many the instruments which these few have devised and often adding its ingenuity to that of the research worker for the benefit of the entire profession of science.

Reducing Needless Variety

So long has the process of duplicating the special apparatus of leading investigators been going on, that the catalogs of the apparatus makers are becoming encyclopedic and the long lists of slightly differing parts quite overwhelming. Each generation of scientific workers has started on its career with quantities of apparatus bequeathed to it by earlier investigators, and to this mass have been gradually added more and more forms without the deletion of obsolete ones. As an illustration of the extent to which this tendency has cluttered up laboratories and storehouses, the Scientific Materials Company points to the fact that 126 different kinds of laboratory gas burners have been in use when the simple Bunsen burner would apparently satisfy most of the requirements. Unfortunately, this variety of burners has represented individual whims rather than essential differences in construction. Many of these have been very inefficient and many have involved differences of form rather than principle—principle seems to have been sadly neglected. To offset such a condition this company has evolved two burners which are universal in their application and are designed particularly with an eye to efficiency. The first of these is an ordinary Bunsen burner modified slightly to increase its efficiency, and the second provides for accurate regulation of the gas as well as the air. Both are adapted to quantity production and hence are relatively cheap.

The case of Bunsen burners cited is typical of a movement covering the entire field of scientific apparatus which is in general progress. American methods demand standardization and quantity production, and the united efforts of the AMERICAN CHEMICAL SOCIETY and the Association of Scientific Apparatus Makers have been actively forwarding a movement to reduce unnecessary variety in laboratory equipment. Certainly nothing more characteristically American nor more important to scientific investigation could be recorded here than this concentrated effort to relieve both makers and users of this burden.

The accuracy with which scientific instruments of precision must be constructed is well illustrated by the care exercised by the Gaertner Scientific Corporation in making a master screw for use on a thread-cutting lathe. This screw is 120 cm. long, and as it is to be used for cutting precision micrometer screws up to a meter in length, it must be of the highest attainable accuracy. In order to do this, the errors of the lead screw of the lathe upon which it was to be cut had to be determined and eliminated. With the help of a microscope and a standard certified meter bar, these errors were read off. A correction bar was then filed whose contour magnified the errors of the lead screw tenfold. This contour bar was used through levers to control the progress of the milling cutter which cut the threads in the rough. The entire operation of this first cutting was carried out in a housing provided with thermostatic control. The result of these painstaking operations was a screw of considerable accuracy but which will again be put through a similar operation in a new recutting lathe under even more carefully controlled conditions to remove its periodic errors.

Quartz Spectrograph

The increasing need in the metallurgical laboratory for quartz spectrographs, used in the precise quantitative analysis of very nearly pure metals, has led the Gaertner Scientific Corporation to modify the instruments for obtaining them to insure sturdy construction and great speed in use. Operation has been simplified by eliminating the scale and micrometer adjustment of the prism and lens and substituting a device operated by a lever which makes possible a setting in any part of the spectrum in a few seconds. The necessity of adjusting the tilt of the plate-holder has been eliminated by building the tilt and curvature into the plate-holder itself.

Balances

An analytical balance in which the pointer is replaced by a beam of light, possessing many advantages in accuracy and speed of weighing, has recently been perfected by Wm. Ainsworth & Sons. The device reads the deflection of the balance beam by means of a ray of light projected from a 6-volt electric lamp to a mirror on the beam, thence to a mirror in front of the index, which reflects it to a third mirror in the top of the balance cabinet, and finally to an index scale in front of the balance mechanism and in the line of vision of the operator. In analytical balances of the usual construction this affords an "optical lever" 5 feet long, or seven times the length of the usual pointer attached to the beam, making it possible to weigh with greater precision, or more rapidly with equal precision by alterations in the center of gravity of the beam to increase or decrease its period of vibration. The elimination of parallax and of eye strain is equally important.

A movable index and a special beam arrest have been built into the newer designs of the analytical balances of Christian Becker, Inc. The movable index makes it possible to weigh accurately, without the necessity of painstaking adjustment of the equilibrium of the arm, by providing a finely adjustable index operated from outside the balance case. This feature permits the easy adjustment of the zero point of the index to coincide with that of the pointer. The new beam arrest insures perfect alignment of the agate bearings at all times and adds to the precision of the balance. It further obviates the necessity of moving the agate edges over the planes on which they rest and thus insures longer life to these vital parts. The "chainomatic" as well as the ordinary analytical balance made by this company is now equipped with these features. The well-known "chainomatic" balance has been further improved by the addition of a rider to the beam for weighing up to one gram. The chain attachment permits exact and quick weighings of 100 mg. in divisions of 0.1 mg. and the addition of the rider for weights up to one gram obviates the necessity for fractional weights. The rider moves over a scale graduated in 100-mg. divisions covering the entire length of the balance beam. Each division is provided with a depression into which the rider fits, thus assuring the accuracy of its position.

Microscopes

Better control of the light passing through specimens and entering the microscope objective has been needed for some time. Several years ago the Spencer Lens Company initiated extensive research into this phase of the subject with a view to the development of a condenser as nearly perfect as possible, so far as its chromatic and spherical corrections were concerned. Two substage condensers, one of N. A. 1.30 and the other of N. A. 1.40, both of which have proved their superior worth, have been the result. With this development came the necessity for accurate manipulation of the substage parts. Such a substage mechanism has been developed and is now being put on all the large research stands made by this company. A new binocular microscope adapted to very low power work and so constructed that the higher binocular objectives of the regular Greenough microscope can be used with it is a recent development in this field. The axes of the eye pieces diverge at a smaller angle than do the axes of the objectives, thereby combining the perspective of the Greenough objectives and of the wider angle of divergence with a narrow and more comfortable angle of vision. The eye pieces stand at an angle of 8 degrees, while that of the objectives is 16 degrees; this 8-degree divergence is much more comfortable for the operator. Some very decided improvements have also been made in the binocular body for single-objective microscopes.

The Spencer Lens Company has also done much along general optical lines. Recently, two 8-inch telescope objectives, very finely corrected, have been completed. Improvements have been made in its regular projection machines and a new line has been put out with which pictures may be projected from standard moving picture film. These films may be changed either manually or automatically. The hand-operated machine is designed particularly for school purposes, and a complete library of pictures coördinated to the regular public school courses in history, geography, nature study, etc., is being collected. The automatic machine is designed principally for use in advertising.

High-Vacuum Pumps

The increasing fruitfulness of investigations conducted at pressures below those obtainable with ordinary vacuum pumps has led to the wider development of mercury vapor pumps, and two new ones have recently been standardized. The Central Scientific Company has developed a mercury vapor pump which operates at a speed comparable with that of any other commercial pump, but requires much less electric power to heat the mercury. This pump is supplied as part of a compactly mounted combination outfit consisting of an efficient fore pump, the mercury vapor pump, and an adjustable electric heater. The W. M. Welch Manufacturing Company has developed a patented pump made entirely of Pyrex glass with which a vacuum of 1×10^{-6} mm. may be easily obtained when it is used in connection with this company's Nelson pump. This mercury vapor pump operating on a volume of 7 liters produced a vacuum of 5×10^{-6} mm. in 20 minutes. The Nelson pump will handle 115 liters (700 cubic inches) of free air per minute at 200 r. p. m. At this speed it will produce a vacuum of 0.02 mm.

A new highly efficient water aspirator for use in producing ordinary vacua required for filtering has been developed by the Central Scientific Company.

Constant-Temperature Baths

An extensive study of the characteristics of constant-temperature apparatus, carried out by the Central Scientific Company, has resulted in a new design for constant-temperature ovens which insures maximum circulation of air, minimum effect of room temperature, and maximum uniformity of temperature both as regards time and distribution throughout the oven space. This has been accomplished without artificial stirring or elaborate thermoregulators. In the course of this investigation it became necessary to design and build an automatic temperature recorder capable of showing clearly on the chart variations as minute as 0.001 degree. This instrument, which was described in the *Journal of the Optical Society of America and Review of Scientific Instruments*, 9, 587 (1924), revealed many important facts about constant-temperature apparatus. The record consisted of simultaneous curves of temperature variation at two selected points in the oven or bath under test, and included automatic testing of the zero points of the galvanometers and of the working current in the potentiometer circuits once every 20 minutes. In the investigation of incubators and constant-temperature drying ovens, this record revealed surprising variations of temperature with time and even more surprising differences in temperature on the same shelf and in various parts of the oven—the temperature in as many as twenty-seven positions in the oven was observed. The marked effect of changes in room temperature upon the constancy of that within the oven necessitated building a constant-temperature chamber which could be controlled at any point between 10 degrees below and 20 degrees above that of the atmosphere. Investigations carried out in this chamber have led to the design of an oven that is practically unaffected by room temperature changes.

Hardness Testing

Hardness testing of metals is increasingly important in industry, and the recent development by the Wilson-Maeulen Company of three new models of its Rockwell harness tester is adding to the facility of such tests. Two of these models are similar to those already in use but of larger capacity. The third was built particularly for testing large pieces such as automobile cylinder blocks. The first two elevate the specimen to apply the initial load, whereas in the other the testing head is lowered onto the piece under test. This makes possible the accurate testing of work that could not be handled by the smaller models.

Box Board Testing

A new instrument for testing box board strength, the invention of C. B. Thwing, has been developed by the Thwing Instrument Company. It operates by measuring the work done in punching a hole through the board by a 2.7-kg. (6-pound) plunger falling 45 cm. (18 inches). For test, a specimen is placed in position and the platen carrying a large weight is lowered to rest upon the board. The plunger is then allowed to fall, its motion being retarded in direct proportion to the strength of the specimen. Measuring weights are lifted by an amount corresponding to the energy still remaining in the falling plunger, which is indicated by a pointer showing the highest movement of these measuring weights. A series of tests on samples of a given board gave readings in very satisfactory agreement.

Consistency Testing

A new device for measuring the consistency of semisolids such as greases, soaps, and creams, which operates rapidly and simply has been put out by the Braun Corporation. The method consists in determining how far a weighted needle will penetrate the substance when dropped from a given height. Tests may be made very rapidly on material in the original containers without the necessity for stopwatch or hand measurements. The device is simple, ruggedly built, and invariably accurate in its results. It may be used for testing finished products and for control at various stages during manufacture.

Viscosity Testing

A new electrically heated and controlled multiple-tube viscometer designed for use with Saybolt viscometer tubes has been introduced this year by the C. J. Tagliabue Mfg. Co. The temperature control consists of a sensitive brass bulb connected by flexible tubing to an expansion coil carrying the moving thermostatic contact, the other being a silver disk intermittently rotated by the action of the relay arm to prevent sticking. The current for heating the bath passes through the tungsten contacts of a relay operated by this thermostatic circuit. Two electric heaters are used, one of 125 watts and the other 500 watts capacity. An automatic throw-out switch controls the operation of these two heaters to secure highly sensitive temperature control at the desired point and rapid heating when needed. The bath is designed to control at one temperature only, since viscosity measurements are universally made at either 100° F. or 210° F. The controls operate within 0.1 degree at 100° F. and within 0.2 at 210° F., and thus insure complete accuracy of the four viscosity measurements which it is possible to carry out simultaneously in this instrument. Other advantages claimed for the control are the elimination of bimetallic and mercury glass thermostats and of sticking of contacts in the relay circuits.

Psychological Tests

Increasing interest in the measurement of human reaction to different stimuli has led the C. H. Stoelting Company to develop a combination of apparatus which permits the experimenter to observe and measure psychological reactions with great speed and accuracy. The basis of this combination is the Dunlap chronoscope operated by a synchronous motor the speed of which is controlled by an electrically maintained tuning fork. Each of the dial divisions of the chronoscope represents one sigma (0.001 second), and it is readily possible to estimate to one-fourth of a sigma. The mere throwing of a switch changes the stimulus and the examiner requires but two fingers of the left hand for operating the master and stimulus keys. The equipment is arranged to give visual, tactual, auditory, or vocal stimulus, and the reactor can respond by either finger or voice.

Another very interesting piece of equipment developed by the same company is known as the Wechsler psychogalvanographe, a rather complicated arrangement for estimating the intensity of emotion by the change in electrical conductivity of the skin. It has been demonstrated beyond doubt that the intensity of an emotion elicited by the stimulus word or otherwise is immediately followed by bodily changes, and these changes can be recorded photographically by means of a very sensitive galvanometer, an adjustable resistance, photographic apparatus, and so on. This equipment, although primarily designed for mental measurements of an indirect character, is not confined to the use of the psychologist, psychopathologist, psychiatrist, and psycho-analyst, but can be used to very good advantage by the physiologist, neurologist, and physician for studying the phenomena of polarization, conductivity of the tissues, reactivity of the blood, body, and so on. With the addition of a thermoelectric couple it can be used for determining minute variations of temperature, imperceptible and unrecordable with the ordinary thermometer.

The study of emotions has led to the development of a device for demonstrating to classes the facial expression of the emotions. This is a model of the profile, devised by Professors Boring of Harvard and Titchener of Cornell based on suggestions from Pederit, consisting of a large basic head with twenty attachable pieces—nine mouths, five eyes, four brows, and two noses. These parts make possible three hundred and sixty different combinations. The study of facial expressions resulting from different emotions has led to the posing of three sets of photographs which depict more or less accurately the facial expressions accompanying some of the better recognized emotions.

High Purity Oxygen Testing

The increasing use of very pure oxygen in industrial work has necessitated the development of a special form of apparatus for the accurate analysis of this gas. The ordinary methods of oxygen analysis using pyrogallol solutions or elementary phosphorus are unsuited for use on the very pure product on account of the liberation of carbon monoxide by the former and the danger of explosive reaction with the latter. The new apparatus for this purpose, designed by Eimer and Amend in coöperation with the Air Reduction Sales Company, consists of a 100-cc. buret calibrated to read in hundredths of a cubic centimeter and a special absorption pipet having a modified capillary to insure the complete return of residual gas to the buret. The absorption reagent consists of small copper spirals covered with a solution of ammoniacal copper chloride. This is prepared by winding 20-gage copper wire into coils on 6-mm. rod to make spirals of 1.5-mm. pitch, and cutting these into 12-mm. lengths. The absorption pipet is filled with these little spirals and an ammoniacal solution of ammonium chloride which readily dissolves the necessary copper on the admission of oxygen. This reagent, after the absorption of a few hundred cubic centimeters of oxygen, is far superior to others for use on the pure gas.

Special equipment for research workers has been developed to a large extent by Eimer and Amend. Recently standardized pieces of this type include special apparatus for handling radium emanation according to Failla for micro-sublimation, for cataphoresis, and for X-ray and other electrical operations. Of special interest to biochemists is the constant-volume type of Van Slyke apparatus for determining gases in blood and other solutions by vacuum extraction and manometric measurement. This apparatus has been standardized with the coöperation of Dr. Van Slyke and his co-workers. Although it is of extreme precision and meets the most exacting research requirements, its operation is so simple as to be preferable to less exact forms for routine laboratory use.

Laboratory Centrifuges

The development of a laboratory basket centrifuge in which the basket is made of high-grade porcelain and the drainage chamber is of glass-enameled cast iron has been accomplished by the International Equipment Company. The basket and its acid-proof drainage chamber may readily be used instead of the ordinary revolving tube heads without alteration of the machine itself. The change from one head to the other requires but a few minutes. A vibrationless stand upon which the centrifuge together with its motor and electrical control may be mounted has also been developed by this company. This stand absorbs practically all the vibration from the machine and is mounted on rubber-tired casters so that the whole may be readily moved from place to place.

Boiler Room Control

The immense cost of power production and the apparently unavoidable low efficiency of steam plants generally has been a constant spur to engineers to minimize the various small losses connected with them. The saving of the slightest percentage of power cost amounts to so much in mass that the reward is extraordinarily great. With such a stimulus it is not remarkable that scientific apparatus makers have devoted much attention to instruments for more accurately controlling the production and utilization of heat. In a similar way the delicacy of many chemical processes involving heat transfer has necessitated the development of accurate devices for recording and controlling temperature.

An electric meter for automatically indicating and recording the percentage of carbon dioxide in flue gases, which can also be used to indicate and record other gases, such as sulfur dioxide, has been perfected by the Brown Instrument Company. This instrument operates on the principle of thermal conductivity in conjunction with a Wheatstone bridge. One electrically heated platinum wire is surrounded by air and another by the gas under analysis. The difference in temperature of these two wires is proportional to the composition of the gas and may be read off as in an ordinary resistance thermometer. This instrument eliminates chemicals that must be replaced, makes possible readings at any desired distance, and indicates continuously, instead of intermittently, the percentage of carbon dioxide in the gas.

The Eddy smoke recorder designed to show a continuous record of the quality of smoke from a stack is among the recent developments of the Gaertner Scientific Corporation. This instrument continuously sucks smoke from the stack, dries it, and deposits the soot in a narrow band on a sheet of white paper. This sheet is constantly rotated and records a complete day's performance in fourteen bands, side by side. The clogging of valves has been overcome by blowing steam through the instrument each time the record is changed.

A recording boiler level gage has been developed by the Foxboro Company to make easier the proper control of water level in a boiler. Both indicating and recording types are available and they may be placed at any convenient point for easy reading. These instruments supplement the ordinary gage glass on the boiler drum and make it much easier for the boiler operator to read his levels in addition to providing an exact permanent record.

Temperature Control

Various types of indicating and recording thermometers are on the market and these are being constantly improved. The C. J. Tagliabue Manufacturing Company has recently brought out a mercury-filled recording thermometer which may be used with a connecting tube as long as 60 meters (200 feet), a special device compensating for changes of temperature over its length. The Wilson-Maeulen Company has added to its line improved forms of resistance bulb electrical thermometers, making them applicable for wide range of industrial uses up to 480° C. (900° F.), an automatic temperature controller of the potentiometer type, and an improved recording pyrometer capable of making single records, duplex records side by side, or in multiple form as many as twelve records on one chart. The Foxboro Company has improved its recording thermometers by a new type of hub for holding the chart in place.

A nonrecording humidity controller in which the wet and dry bulb scales are separate and calibrated for the entire range of the instrument has been brought out by the Foxboro Company. The temperature elements of this instrument are replaceable as a unit and easily accessible for overhauling. No rubber tubing or other parts subject to deterioration are included, and the instrument may be used in processes and operations where continued and severe strains are met.

Oil Prospecting

The Eotvos balance for detecting and mapping oil deposits has been greatly improved as to ease of operation and sturdiness of construction for use in the field by the Gaertner Scientific Corporation. The laborious nature of the operation of old forms of this apparatus greatly discouraged its wide use, but with the new form it is possible to carry out a complete set of observations at a single station in an hour.

Rubber Aging Tests

The apparatus described in THIS JOURNAL, **16**, 711 (1924), and **17**, 860 (1925), by Bierer and Davis, for the accelerated aging of rubber is being offered by the Emerson Apparatus Company. It consists essentially of a bomb in which the rubber under test may be heated in the presence of oxygen under pressure. In this way it is possible to secure the effect of several years' natural aging in a few hours.

A new multiple stirrer for the simultaneous stirring of six beakers has been developed by the L. E. Knott Apparatus Company. The stirrers are operated by a 110-volt (either a. c. or d. c.) electric motor and are driven through friction drives in such a way that the speed of each may be regulated independently of the others.

Conclusion

Many of the makers of equipment of this type have been at work on apparatus which they are not yet ready to offer the public. Others report that their activities during the past year have been devoted entirely to mechanical improvements in their manufacturing processes or products and that the results have therefore been of little general interest. The results of the labors of these essential servants of science are manifest in the immense amount of accurate and important research work that is being continuously published in this country. The increasing activity of research in all lines in this country is placing upon them a serious responsibility which they will not fail to assume. Their opportunities for service in this age of the "Fifth Estate" are boundless.

Making Stronger Concrete

Water is an important ingredient in concrete. Experiments just completed at the Bureau of Standards show that this is just as true with the new quick-hardening high-alumina cements as with Portland cement.

The Bureau of Standards finds it important to select sand and gravel in proper size gradation, since less water is required to make the concrete workable and a greater strength results. In one experiment a decrease of 1 per cent of water was found to increase the strength as much as 26 per cent.

Progress in the Domestic Manufacture of Dyes and Other Synthetic Organic Chemicals during 1924

By W. N. Watson

U. S. Tariff Commission, Washington, D. C.

ONE of the more important results of the World War has been the progress of the leading nations of the world toward industrial independence. Industrial development has been nothing short of phenomenal, and chemical manufacturing has been especially prominent in this unprecedented expansion. The intimate relation between the manufacture of dyes and coal-tar chemicals on the one hand and of high explosives and poisonous gases on the other has emphasized the necessity of a domestic chemical industry, not only as a source of supply of essential products in time of peace, but also as a vital factor for our national defense and security in time of war. Great Britain, France, Italy, Japan, and the United States have either established or expanded their existing industries many times and now produce a large number of dyes and synthetic organic chemicals on a commercial scale. A study of the progress in this industry since 1914 will show that in important respects the United States has outdistanced these other countries. The progress of the domestic industry within the past seven years is probably unparalleled.

Pre-War Situation

Dyes—Prior to the war the dye industry of the United States was in no sense self-contained, consisting largely of assembling plants for the manufacture of a limited number of dyes from German-made intermediates. The output of dyes in 1914 by seven firms was 6,619,729 pounds, valued at \$2,470,096. In that year the industry employed 528 persons and represented a capital investment of \$3,386,212. The imports of coal-tar intermediates in 1914 exceeded 10 million pounds with an invoice value of over \$1,000,000.

Intermediates and Other Coal-Tar Chemicals—A small part of the domestic requirements of aniline was produced by one company after 1910. Salicylic acid, used as a medicinal and in the manufacture of acetyl salicylic acid, methyl salicylate, and other salicylates, was made by a single firm. Small amounts of benzoic acid, used chiefly in medicinals and in the manufacture of sodium benzoate for a food preservative, were also produced. Phenol was extracted from coal-tar but in insufficient quantity to meet the domestic demand. Among other finished coal-tar products manufactured were synthetic phenolic resins and saccharin.

Synthetic Organic Chemicals—A small number of synthetic organic chemicals of non-coal-tar origin were produced in addition to those obtained by the distillation of wood. Among these were chloroform, ether, formaldehyde, acetaldehyde, amyl acetate, and vanillin.

Summarizing the pre-war situation, it may be said that this country depended largely upon Germany and to a lesser extent upon other countries for its requirements of dyes and other synthetic organic chemicals. Domestic production at that time largely consisted of assembling finished products from imported raw materials and in the manufacture of a few products on a comparatively large scale.

Developments in Period 1914 to 1924

Shortly after the outbreak of the war the supply of imported dyes and other synthetic organic chemicals was almost entirely shut off. Following the exhaustion of the stocks on hand there developed an acute dye famine, which at one time threatened the activity of the vast textile industry. Many pharmaceuticals essential for the national welfare were not obtainable. The prices of dyes and other organic chemicals increased many times over their pre-war levels and for a time many products were not obtainable at any price.

This condition led to the establishment of the manufacture of intermediates and dyes on a large scale, as well as of other finished coal-tar products, including flavors, perfumes, medicinals, synthetic tanning materials, and, in addition, a variety of synthetics of non-coal-tar origin. The manufacture of synthetic phenol, picric acid, TNT, and certain poison gases was also developed on a very large scale, large quantities of explosives being furnished the Allies prior to the entry of the United States in the war. Since 1917 annual progress of this important branch of the chemical industry has been published in detail in the annual census issued by the United States Tariff Commission.

By 1923 this remarkable expansion had reached such a point that our domestic output of dyes supplied about 96 per cent of the consumption, and there was an exportable surplus of certain dyes amounting to about 18 million pounds. In 1923, the peak year of production, the sales of domestic dyes by 88 firms exceeded 86 million pounds, with a value of over \$47,000,000. Sales of the other finished coal-tar chemicals in 1923 reached nearly 29 million pounds, with a value of \$19,000,000.

Because of the greater interest in the progress of the coal-tar chemical industry, the rapid development in the manufacture of organic chemicals of non-coal-tar origin has been comparatively unnoticed. It is highly probable that this branch of the chemical industry will continue to expand and that new products of great economic value will be placed on the market by domestic firms. The progress up to 1923 is indicated by a production during that year of over 90 million pounds of these chemicals. The total sales were nearly 68 million pounds, valued at nearly \$14,000,000.

Great credit is due to the American engineering and chemical profession, as well as to the liberal investment of capital in the establishment and subsequent development of the synthetic organic chemical industry. A factor which aided the early progress and growth in this field was the limited competition from foreign imported products during and immediately following the war.

Under the "Trading with the Enemy Act" (October, 1917), the President, on February 14, 1918, issued a proclamation declaring that certain articles of commerce should not be imported from specified countries except by license granted in accordance with prescribed regulations. Dyes and chemicals were included in this proclamation. In the spring of 1919 (February) Swiss dyes (non-enemy origin) were imported under license and in the fall of 1919 licenses were granted for the importation of German dyes. Under Title V of the Emergency Tariff the importation of dyes and other synthetic organic chemicals was placed under license control (May 27, 1921) "Dye and Chemical Control Act of 1921." This continued until the date of the passage of the Tariff Act of September 21, 1922.

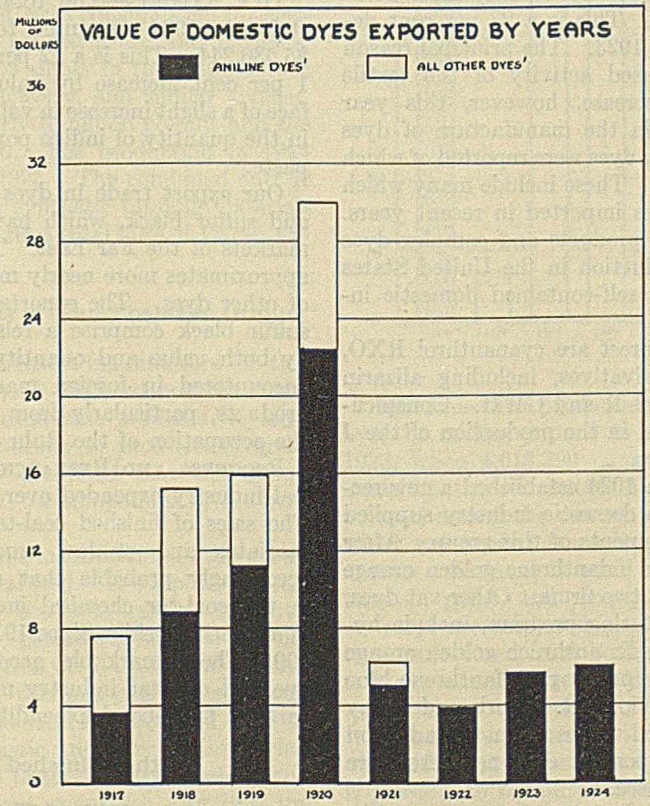
Under the Act of 1922 coal-tar chemicals received special protection under Paragraphs 27 and 28. The ad valorem rate on dyes and finished coal-tar products within Paragraph 28 was 45 per cent, with the proviso that for two years following the date of the passage of the act (September 22, 1922) the ad valorem rate was 60 per cent. On intermediates, Paragraph 27, the ad valorem rate was 40 per cent, with the proviso that for two years following the date of passage of the act the ad valorem rate was 55 per cent. The specific duty was 7 cents per pound. In the case of coal-tar dyes this duty is based on standards of strength established by the Secretary of the Treasury. This act provided that the ad valorem rate of duty on any imported coal-tar product coming within Paragraph 27 or 28 is based upon the American selling price (as defined in sub-division (*f*) of section 402, Title IV) of any similar competitive article manufactured in the United States. A product was defined by the act as similar or competitive with any imported coal-tar product which accomplishes results substantially equal to those accomplished by the domestic product when used in substantially the same manner. In case a similar competitive article is not manufactured in the United States, then the ad valorem rate is based upon the United States value as defined in subdivision (*d*) of section 402, Title IV, which is the selling price in the United States of the imported article less certain statutory deductions, including profits, general expense, cost of insurance, transportation, and duty.

Another factor which aided the domestic industry by reducing competition and increasing exports of dyes during 1923 was the occupation of the Ruhr by the French, which resulted in diminished production of dyes and other products by German firms.

Crudes

The total production of coke in 1924 was nearly 43 million tons. Of this total about 78 per cent was made at "by-product ovens" and 22 per cent at "beehive ovens." The increase in the proportion made at by-product ovens is of significance. In 1913 about 22 per cent of the coke was from the by-product ovens and 73 per cent from the beehive ovens. The beehive coke industry may now be looked upon as an auxiliary source which is available when the output of the by-product ovens is inadequate. The large installations of by-product ovens have resulted in the conservation of natural resources owing to the increased output of valuable by-products, including ammonium compounds for fertilizer and other uses, gas for industrial heating and municipal lighting, and a supply of tar far in excess of the requirements of the domestic coal-tar chemical industry, as well as for road building, roofing materials, and certain other uses.

The output of tar for 1924 was about 470 million gallons. About 90 per cent of this total was from by-product ovens. Of the total production of tar, nearly 54 per cent was sold, of which 193 million gallons was distilled, equal to nearly 42 per cent of the total production; the remaining 58 per cent was largely consumed as fuel. Of the 42 per cent distilled, only a small part was separated into refined products, such as phenol, cresylic acid, naphthalene, and anthracene, on account of the demand for partly refined products, such as solvents and soft pitches for road building, roofing, and other uses. In the case of the light oil stripped from the coke oven gas a similar situation exists; only a part is distilled into refined benzene, toluene, and xylene, on account of the demand for such partly refined products as motor fuel and solvents. Increases in the production of benzene, toluene, and solvent naphtha were recorded in 1924. The output of phenol (from tar), cresylic acid, and creosote oil is still far below domestic requirements.



[1] The domestic exports of dyes, as shown by the Commerce Department, are divided into three groups—(1) aniline dyes, (2) logwood extract, and (3) all other dyestuffs.

The third classification may include both natural dyes (other than logwood extracts, shown separately) as well as coal-tar dyes. Since logwood extract, however, is the most important natural dye exported from the United States, it is reasonable to assume that a considerable portion of "all other dyes and dyestuffs" represents coal-tar dyes. In 1922, however, the Commerce Department adopted a new classification. Coal-tar dyes were grouped under coal-tar finished products and were divided into (1) color lakes, and (2) other colors, dyes, and stains.

Intermediates

The production of over 186 million pounds of intermediates in 1924 represents nearly a 20 per cent decline from that of 1923. There were marked decreases in the output of the bulk intermediates such as aniline, β-naphthol, and H acid, normally consumed in large amounts in dye manufacture. Notable progress, however, is indicated by the relatively small decrease, and in many cases conspicuous increases, in the output of the more complex intermediates used in the production of the fast and specialty type of dyes and other finished coal-tar products.

Rubber Accelerators—The rapid expansion in the variety and amount of intermediates used for the acceleration of rubber is a development of importance. The use of accelerators results in great economy in time for the rubber manufacturers. It has been estimated that about $80,000,000 additional capital[1] would be needed if organic accelerators were not used.

Phenol—The output of phenol in 1924 was 10,521,944 pounds, an increase of over 200 per cent over that of 1923. In three years the production has increased more than eight times that in 1922 of 1,285,978 pounds. The largest use of phenol is in the manufacture of synthetic phenolic resins, such as Bakelite, which is used for electrical insulation material and for molded parts for automobiles and radios. There are two kinds of phenol: (1) natural phenol, obtained from coal tar by extraction and purification; and (2) synthetic phenol, made from benzene. The increase in the output of phenol in 1924 was largely that of the synthetic product. It is apparent that the synthetic product will continue to be a factor of increasing importance in supplying our domestic consumption, which is estimated at about 11 million pounds per year.

Phthalic Anhydride—Phthalic anhydride, with a record output of 2,787,308 pounds, recorded one of the most striking increases among the intermediates in 1924. It is made by the catalytic oxidation of naphthalene, an American discovery and development, and is used in the direct production of dyes and in the preparation of synthetic anthraquinone, the latter being used for making alizarin and certain vat dyes. The recessions in price of phthalic anhydride since 1917 constitute one of the most notable declines in the entire field of intermediates. From an average price of $4.23 per pound in 1917, it dropped to 24 cents per pound in 1924, a figure below that of 1914 when our entire consumption was imported. The current price in May, 1925, was 18 cents per pound.

Significant amounts of phthalic anhydride were exported in 1924, which indicates that this intermediate is being produced on an international basis.

Anthraquinone—Anthraquinone is produced in the United States by two methods: (1) the oxidation of anthracene obtained from coal tar; this method was first used in the preparation of anthraquinone and is the principal commercial method in use by both Germany and Great Britain; (2) synthetically from phthalic anhydride and benzene.

Anthraquinone is an intermediate of high importance on account of the increasing consumption of the fast vat dyes largely used on cotton, and of certain alizarin derivatives including the acid alizarins used for wool. The out-

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[1] Geer and Bedford, This Journal, 17, 396 (1925).

put of anthraquinone in 1924 was 638,755 pounds, about three-fourths of which was made by the synthetic process, compared with about one-half in 1923. The progress in the manufacture of synthetic anthraquinone has solved what, in 1919, was one of the principal problems of the domestic dye industry. At that time the supply of anthracene was inadequate, not on account of the lack of anthracene in domestic tar, but because the removal of anthracene oil leaves a hard pitch, which has a limited market in this country. The synthetic product has the advantage of greater purity and it now promises to supply the entire domestic requirement.

New Intermediates—Over sixty products were reported in 1924, most of which were manufactured for the first time in the United States during that year. These new products represent commendable progress. They are used in the manufacture of new dyes, accelerators for rubber, synthetic medicinals, and a variety of other finished coal-tar products.

Two notable products produced in 1925 are hexahydrophenol and tetrahydronaphthalene, known in the trade as Hexalin and Tetralin. Hexahydrophenol is a high-boiling solvent and, although insoluble in water, dissolves in aqueous soap solutions. These colloidal solutions possess emulsifying and detergent properties.

Tetrahydronaphthalene, made by the hydrogenation of naphthalene, is also a high-boiling solvent which has promise of application as a solvent in the oil, paint, and varnish industries. It is also added with Hexalin to soaps.

Dyes

The production of coal-tar dyes by seventy-eight firms in 1924 was 68,679,000 pounds. This is a 27 per cent decline from that of the peak year 1923. The principal reason for the decline was the decreased activity of the textile industry. In spite of this decrease, however, this year brought notable advancement in the manufacture of dyes in the United States. Over sixty dyes were reported of which no output was recorded in 1923. These include many which have been among the chief dyes imported in recent years. The additions include specialty products and complex dyes of high fastness, and their production in the United States is an important step toward a self-contained domestic industry.

Among new products of interest are cyananthrol RXO, as well as several alizarin derivatives, including alizarin emeraldol G and alizarin rubinol R and GWH. Conspicuous increases have been recorded in the production of the J acid and the anthraquinone dyes.

The production of vat dyes in 1924 established a new record of 1,821,319 pounds. The domestic industry supplied about 55 per cent of our requirements of this group. After several years' intensive research indanthrene golden orange RRT and G are now made by two firms. Other vat dyes, recently added to our manufacturing program, include hydron scarlet BB, hydron orange R, anthrene golden orange 4 R, ponsol brown G and R for printing, sulfanthrene blue GR, indanthrene red BN, and violet R. Work under way in this country may be expected to result in the addition of a considerable number of important dyes not heretofore manufactured in the United States.

Assuming that consumption equals production plus imports minus exports, the domestic industry supplied, in 1924, about 95 per cent of the apparent consumption.

The weighted average price of all dyes sold in 1924 was nearly 2 per cent less than the average of 1923. The average price for 1924 was 54 cents compared with $1.26 in 1917, and since the latter date there has been a conspicuous expansion in the manufacture each year of the faster high-cost dyes. The average sales price of indigo was 22 cents per pound in 1924. The current price in May, 1925, was 14 cents per pound, a figure below that in 1913 when our dye supply was imported. Available prices from different countries indicate that the United States consumers of indigo are paying less for domestic indigo than consumers in other countries are paying for their indigo.

Dye Imports—The total imports of dyes in 1924 was 3,022,539 pounds invoiced at $2,908,778, a slight decrease from that of 1923. Vat dyes represented nearly 50 per cent of all dyes imported. Concerning the countries of origin, 50 per cent came from Germany, 30 per cent from Switzerland, 5 per cent from Italy (the latter figure probably represents reparation dyes of German manufacture, reëxported from Italy), 3 per cent from France, 4 per cent from England, and 8 per cent from all other countries.

Effect of Reduction of Duty on Imports—On September 22, 1924, under the provisions of the Tariff Act of 1922, the ad valorem rate on dyes and other finished coal-tar products (paragraph 28) was reduced from 60 per cent to 45 per cent. The specific duty remained at 7 cents per pound. A comparison of the imports before and after the tariff reduction on September 22 shows a rapid increase in the monthly imports after the reduction in duty and indicates increased competition from foreign-made dyes. The average monthly import of dyes from October 24, 1924, to April, 1924, inclusive, was 452,453 pounds. This is a 152 per cent increase over the monthly average of the first nine months of 1924 preceding the tariff reduction on dyes. These dyes are almost entirely of German and Swiss manufacture and consist largely of the higher cost types.

Dye Exports—The total exports of dyes, colors, and stains in 1924 amounted to 15,713,428 pounds valued at $5,636,244. This is a 12 per cent decline in quantity and a 1 per cent increase by value. The decline in quantity in face of a slight increase in value is probably due to an increase in the quantity of indigo powder exported in place of indigo paste.

Our export trade in dyes consists very largely of indigo and sulfur black, which have been shipped mostly to the markets of the Far East. The manufacture of these items approximates more nearly mass production than in the case of other dyes. The exports of dyes other than indigo and sulfur black comprise a relatively small part of the total by both value and quantity. Keen competition has been encountered in foreign markets from German and Swiss products, particularly from the former, since the effect of the occupation of the Ruhr in 1923 has disappeared.

Progress and Research—The domestic coal-tar chemical industry expended over $2,000,000 in research in 1924. The sales of finished coal-tar products (exclusive of intermediates and crudes) amounted to $56,000,000. It is accordingly probable that expenditures for investigations in the coal-tar chemical industry have been greater than in any other field. Since 1917 they have exceeded $25,000,000. The remarkable accomplishments of the domestic dye and coal-tar industry must be attributed, in no small part, to the liberal expenditures in research.

Other Finished Coal-Tar Products

Medicinals—Each year has recorded progress of high importance in the domestic manufacture of medicinals. The total output of coal-tar medicinals in 1924 amounted to 2,967,944 pounds. Arsphenamine, known also as salvarsan and as 606, used for combating syphilis, is one of the most valuable medicinals of this group. The output by seven firms in 1924 was 555 pounds. Arsphenamine of domestic manufacture was sold to the Government in 1925 (fiscal year) for less than 10 cents per ampoule, whereas prior to the war, when this country depended on a German supply, the retail price was $3.50 an ampoule. The sales of neoarsphenamine in 1924 were 2981 pounds, valued at $959,473.

Luminal and luminal sodium, hypnotics used in nervous insomnia, are also very important in the treatment of epilepsy, and were manufactured for the first time in 1924.

Perfumes—The output of this group in 1924 reached 1,895,267 pounds, a 39 per cent increase over that of 1923. Diethyl phthalate, used under a special formula as an ethyl alcohol denaturant, ranked first in quantity of production, with an output of 1,676,911 pounds and a total sales of 1,750,510 pounds, valued at $673,517. Diphenyl oxide and phenylethyl alcohol recorded increased production over that of 1923. Imported phenylacetic aldehyde supplies a large part of our consumption, whereas our entire requirements of artificial musks are imported.

The production of flavors was 1,750,555 pounds, an increase of 292,531 pounds over that of the previous year. The sales in 1924 were 1,691,863 pounds, valued at $1,471,089. Substantial increases were shown in the production of methyl salicylate and coumarin.

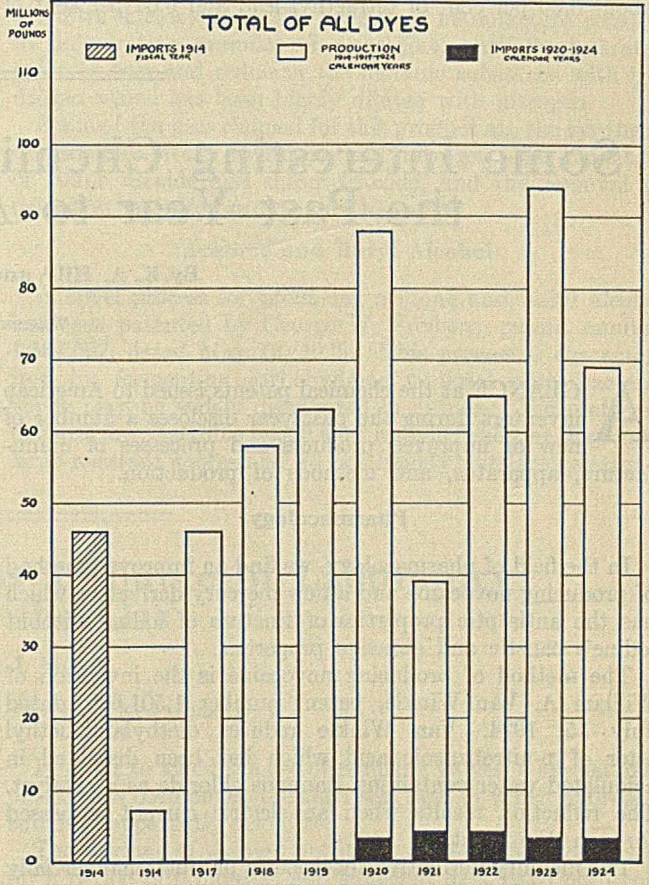
Synthetic Phenolic Resins—This industry is distinctly an American development and has resulted only from the most careful research and engineering skill. Synthetic phenolic resins are used in large quantities by practically all American automobile manufacturers in the construction of many different parts of the automobile. The increase in the demand for radio equipment has led to a large increase in the application of these resins for the construction of radio apparatus. There is also a large consumption for electrical insulating materials and for varnishes and lacquers. They are used as a substitute for amber in the manufacture of pipe stems, cigaret holders, jewelry, and similar articles. In 1922 the production was nearly 6 million pounds and the sales were valued at $4,315,196. The production in 1924 shows an increase over that of 1923. The combined output of synthetic phenolic resins and synthetic tanning materials in 1924 was 12,778,115 pounds, with a total sales of 12,745,458 pounds valued at $8,818,014.

Synthetic Organic Chemicals of Non-Coal-Tar Origin

The developments in the domestic manufacture of this group of products have been among the most notable in the chemical industry, and further expansion promises to result in the manufacture of a large variety of products of great commercial value. It is freely predicted that this group may rival in importance the coal-tar compounds in the near future.

Since the outbreak of the war the manufacture of this group of chemicals has expanded several fold. It supplies at present our requirements for many products used as solvents, pharmaceuticals, disinfectants, perfumes, flavors, rubber accelerators, and other items. One of the principal reasons for the increase in output of the non-coal-tar synthetic organic chemicals has been the demand for improved solvents for use in the nitrocellulose plastic and varnish industries. Such solvents as ethyl acetate, butanol, butyl acetate, and amyl acetate are produced in large quantities. In 1924 the output of synthetic organic chemicals, other than those derived from coal tar, was 115,817,865 pounds compared with 90,597,712 pounds in 1923. The sales in 1924 amounted to 85,933,461 pounds, valued at $20,604,717.

Acetylene Derivatives—Increases were recorded in the output of acetaldehyde and of aldehyde-ammonia in 1924. During that year one firm produced acetaldehyde and some of its derivatives by methods similar to those developed during the war at Shawinigan Falls, Canada. In this process acetylene made from calcium carbide is converted to acetaldehyde in the presence of sulfuric acid and a mercury salt. Acetaldehyde may be converted to acetic acid by oxidation in the presence of a catalyst. This process has been operated successfully on a large scale for some time in Canada. A number of other products may be made from acetylene and it is expected that the production of acetaldehyde is only a step in the manufacture of other acetylene derivatives.



Butanol—The production of this solvent by a single firm, over 14 million pounds in 1924, was a large increase over 1923, when 4,613,396 pounds were produced.[2] Butanol is made by the fermentation of corn. This process was developed during the war on account of a shortage of acetone which was needed as a solvent for nitrocellulose and cellulose acetate. Butanol is used as a solvent and vehicle in the varnish, paint, and pyroxylin industries. A large amount of butyl acetate, used as a solvent for pyroxylin plastics, is manufactured from butanol. It is reported that butanol is to be manufactured in this country starting with natural gas as a raw material.

Petroleum Derivatives—By cracking methods carried out under exact conditions in the presence of a catalyst it is possible to obtain unsaturated hydrocarbons from which can be made secondary propyl, butyl, amyl, and hexyl alcohols, and also the higher molecular weight ketones. Developments in the United States during 1924 promise the establishment of the manufacture of this group of products in the United States. Isopropyl alcohol is already manufactured on a commercial scale.

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[2] Boston News Bureau, February 14, 1925.

FORMALDEHYDE—The large output of synthetic phenolic resins is reflected in an increase in the production of formaldehyde. This product also has extensive application in the preparation of rubber accelerators.

PHARMACEUTICALS—A new pharmaceutical manufactured for the first time in 1924 was amytal (isoamylethylbarbituric acid). The production of synthetic isomenthol, which was also started in 1924, is of special interest. This country has been dependent upon imports of natural menthol from Japan, as American peppermint oil was too high priced for use for menthol manufacture.

TETRAETHYL LEAD—Ethyl gasoline is gasoline containing about 0.06 per cent of tetraethyl lead and 0.04 per cent of ethylene dibromide. The tetraethyl lead is used as an antiknock compound and it also decreases the reaction velocity of combustion and makes it possible to use engines of a higher compression ratio with an increase in the mileage per gallon of gas consumed. The general distribution of ethyl gasoline to the public was discontinued in May, 1925, until the question of the possible health hazard involved in its use has been settled. From July, 1924, to May, 1925, about 1,750,000 pounds of tetraethyl lead were manufactured. The use of tetraethyl lead or of a product giving similar results will undoubtedly increase in the future and permit greater efficiency in the design and operation of automobile engines.

Some Interesting Chemical Patents Issued during the Past Year to American Inventors

By E. A. Hill[1] and Francis B. Leech[2]

WASHINGTON, D. C.

A GLANCE at the chemical patents issued to American inventors during the past year discloses a number of new or improved products and processes of manufacture, apparatus, and methods of production.

Pharmacology

In the field of pharmacology, we find an improved method of producing novocaine and a new mercury derivative which has the antiseptic properties of tincture of iodine without iodine's caustic and abrasive properties.

The method of producing novocaine is the invention of William A. Van Winkle, patent number 1,501,635, dated July 15, 1924. Van Winkle reduces diethylaminoethyl ester of *p*-nitrobenzoic acid which has been dissolved in acidulated water containing stannous chloride as a catalyst. The reduction results when an electric current is passed through the solution.

The mercury derivative therapeutic product commercially known as Mercurochrome is the invention of Edwin C. White, patent number 1,535,003, dated April 21, 1925. This product comprises the chlorine-free monomercury derivative of dibromofluorescein. It is prepared by reacting with mercuric acetate on an aqueous suspension of dibromofluorescein.

Mineral Oils

Mineral oils have received the attention of many inventors, and patents have issued for improved processes of cracking to C. P. Dubbs and E. M. Clark.

In the Dubbs process as set forth in patent 1,522,425, dated January 6, 1925, a body of hydrocarbon oil is converted into low boiling point hydrocarbons by passing the oil through a continuous elongated passageway maintained at a cracking temperature. The oil is then vaporized in an enlarged chamber, after which the insufficiently cracked vapors are condensed in a reflux condenser. The process makes use of super-atmospheric pressures.

Clark, as disclosed in patent 1,525,916, dated February 10, 1925, subjects the hydrocarbon oils to be converted into lower boiling point hydrocarbons to a temperature above 680° F., at a rate such that no substantial portion of the desired low boiling point products are formed during the heating. The heated oil is then compressed to a pressure at which the inconverted oil is in the liquid state and the heated oil is retained under such pressure without reduction in temperature below 680° F., to effect conversion thereof.

Plastics

Carlton Ellis and Norris Boehmer have recently patented a series of inventions relating to chlorinated rubber and processes of making the same. These patents are numbered 1,544,529 to 1,544,535, inclusive, all dated June 30, 1925. The new product is a plastic mass containing chlorinated rubber and a substantial amount of liquid-free chlorine, the latter serving as a plasticizing agent for the normally solid chlorinated rubber.

Insecticides

Efforts to exterminate the boll weevil have brought forth a new method of manufacture of calcium arsenate, which is extensively used as an insecticide. This invention is based on the discovery that such arsenates may be commercially produced by the air oxidation of a mixture of white arsenic and the oxide or hydroxide of calcium or magnesium. Burned lime is slaked with water to a fine powder and mixed with powdered arsenic to form a mud and then oxidized in a reverbatory or other furnace. The method described has been patented by Joseph F. Cullen, patent numbers 1,532,577 and 1,532,578, dated April 7, 1925.

Electrochemistry

Electrochemistry has yielded several advances for which patents have been granted. Among these are a method of deposition of nickel and cobalt or their alloys, patented by Charles P. Madsen, patent 1,513,119 of October 28, 1924, and a method of effecting organic reactions, patented by Arthur W. Burrell, number 1,536,419, dated May 5, 1925.

Madsen uses a rotating cathode of fusible metal which can be removed by heating the finished article so as to melt the original cathode. Nickel tubes can be thus readily formed. A colloidial solution of the metal salt is employed.

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[1] Examiner, U. S. Patent Office.

[2] Patent lawyer.

In the Burrell process an electric current is caused to flow through an aqueous electrolyte, on the active surface of which is maintained a moving film of an organic liquid to be transformed, the organic liquid being substantially insoluble in, and immiscible with, the electrolyte. As an example, nitrobenzene is reduced to aniline, using a cathode having a tin surface and an electrolyte of sulfuric acid.

Rubber Accelerators

Several accelerators for use in rubber vulcanization have been patented during the past year. Of interest in this line is the patent to John Young, number 1,538,076, issued May 10, 1925. Young proposes to promote the vulcanization of rubber by incorporating therewith a small amount of a mixture of ditolyl-substituted guanidines including di-*o*-tolylguanidine and di-*p*-tolylguanidines in which the *o*-tolylguanidine predominates.

Varnish

A new phenolic resin varnish of the Bakelite type has been recently patented by Harold C. Cheetham, patent number 1,528,006, dated March 3, 1925. Cheetham calls for a liquid coating composition comprising a phenolic resin of a potentially reactive type together with an organic solvent therefor and furfural.

Coal Distillation

A patent was recently issued to Elmer J. Crossen, number 1,522,421, dated January 6, 1925, for an improved apparatus for the destructive distillation of coal. This apparatus consists of a plurality of ovens, having combustion chambers arranged longitudinal to the oven walls. Means are provided for supplying gas for ignition purposes to the chambers, the length of the gaseous stream in the chambers being adjustable.

Catalyst and Absorbent

A catalytic and absorbent material produced from metallic hydroxide gels has been patented by Robert E. Wilson, number 1,540,448, dated June 2, 1925. This catalyst is essentially pyrophoric iron, which is highly porous and infrangible, and in which the pores of the metallic substance are ultra-microscopic. The process of manufacture consists in dehydrating granules of a gel-like, partially hydrated oxide of iron and reducing the metallic substance with hydrogen which has been highly diluted with nitrogen.

Some of the uses claimed for this product are the synthesis of ammonia from hydrogen and nitrogen, the oxidation of sulfur dioxide and sulfur trioxide, and the removal or oxidation of sulfur compounds to gases.

Acetone and Butyl Alcohol

A novel process for producing acetone and butyl alcohol has been patented by George W. Freiberg, patent number 1,537,597, dated May 12, 1925. This process is characterized by fermenting carbohydrate material with bacteria which may be widely distributed in nature. The preferred bacteria are anaërobic bacilli with rounded ends, as they form large resistant spores and do not liquefy nutrient gelatin.

Liquid Hydrogen Sulfide as a Source of Laboratory Supply of the Gas[1]

By Charles J. Moore

Hunter College of the City of New York, New York, N. Y.

The notion seems to be prevalent that to liquefy hydrogen sulfide is a risky undertaking on account of the instability of the substance and the possibility of violent thermal dissociation. This, together with the fact that it attacks reducing valves, such as are commonly used on tanks of compressed gases, is probably the reason manufacturers have made no attempt to produce the liquid product until very recently.

It is well established that the heat of formation of hydrogen sulfide is positive, and this guarantees that there can be no sudden, extensive thermal dissociation at ordinary temperature. However, when the writer installed an outfit using the liquid as a source of supply, he was well aware of the possibility of slow, continuous dissociation resulting in excessive pressure due to the hydrogen liberated. In order to guard against danger, analyses were made of the gas, and even after standing 6 months it was found to contain less than 0.25 per cent of hydrogen. A pressure gage attached to a cylinder for 4 months showed an increased pressure of less than one pound. The pressure in a cylinder containing 20 pounds of the liquid at 100° F. is 281 pounds per square inch, and at 150° F. it amounts to 500 pounds. The cylinders are said to have been tested to 3000 pounds. It therefore seems safe to use the liquid. Samples analyzed by the writer seem to be very pure, containing, in addition to the small amount of hydrogen mentioned above, traces of aniline and carbon disulfide from which substances it is produced as a by-product in the manufacture of diphenylthiourea.

In order to avoid the use of reducing valves, a special gasometer has been devised using a seal fluid in which hydrogen sulfide is apparently insoluble.

The working of the new outfit has been carefully observed for a period of 6 months, and sufficient data have been collected to justify the following comparisons: The initial cost of the system is more than double the cost of one Parsons generator. To generate 1 pound of hydrogen sulfide, 2.6 pounds of iron sulfide and 6 pounds of hydrochloric acid are required, costing between 60 and 75 cents. The liquid can be purchased in small quantities for 50 cents per pound. The pressure in the gasometer can be regulated at will and maintained constant. The gasometer can be filled from the high-pressure cylinder in a few moments, and an empty cylinder can be replaced in less than 5 minutes. To clean and refill a large generator is a disagreeable task, detrimental to health, and requires considerable time. Generators give little indication that the charge is nearing exhaustion until there is a sudden drop in pressure, which invariably happens when the gas is urgently needed. The disposal of the spent generator liquid is another matter worthy of consideration, since it is injurious to plumbing and increases to some extent the poisonous component of sewer gases. In cold weather, especially if sulfuric instead of hydrochloric acid is used, generators become badly clogged with crystalline iron salts, which are often difficult to remove.

The writer ventures to predict that the days of the hydrogen sulfide generator are numbered and in a short while will disappear from the chemical laboratory.

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[1] Received March 27, 1925.

Twenty-Five Years of Rubber Chemistry[1]

By William C. Geer[2]

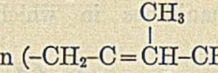
The B. F. Goodrich Co., Akron, Ohio

OUR knowledge of the chemistry of rubber and its various products has grown coincidentally with the growth of rubber factories. In 1900 these factories were few, and the chemist as a forward-working research man was rare in the industry. Since then, factories and research laboratories have grown; and during this twenty-five-year period, not only in these commercial, but somewhat also in university, laboratories many searching investigations have been performed. Thus our knowledge of the chemistry of rubber is mainly derived from the researches of the last twenty-five years.

If the reviewer were to incorporate in one paper references even to the majority of these workers, it would become necessary to expound the work of each, with differences of opinion and findings clearly delineated. In particular, the reviewer's own judgment of the weight to be given each would need precise statement. Such a method would extend the review to the size of a small volume. He has, therefore, attempted to outline only the generally accepted essential facts of rubber chemistry as they have been developed during the past twenty-five years.

Chemistry of the Rubber Hydrocarbon

What is rubber? That is an old question. Crude rubber had been purified and analyzed[1,2,*] prior to 1900; it had been distilled as early as 1826, and several hydrocarbons, including isoprene, C_5H_8, and caoutchene or dipentene, $C_{10}H_{16}$, were isolated from the distillate. The carbon-hydrogen ratio, C_5H_8, was known and accepted before 1900. Likewise, chemists knew the fact of chemical unsaturation, and it was believed from optical measurements[3] that there were one and one-half double bonds for each C_5H_8 group, and accordingly the fundamental group in rubber was believed to be $C_{10}H_{16}$.

Rubber has been a difficult substance to examine from the standpoint of the organic chemist, for it is colloidal; molecular weight measurements are of no account; it has no constant melting point, and decomposes when distilled. It was known for many years that it reacted with the halogens, oxygen, sulfur, and nitric acid. It had been chlorinated[3] and an impure bromide was known. The addition of sulfur refers back to the important date of 1839, when Charles Goodyear discovered that sulfur affected rubber, making it less sensitive to heat and cold; but until the work of Weber,[4] in 1902, little was definitely postulated regarding the real action of sulfur upon rubber. The chemistry of these reactions is now more clear, for it is well established that two bromine atoms add to each C_5H_8 group forming $(C_5H_8Br_2)_x$ (or as it used to be written, $C_{10}H_{16}Br_4$,[4a] whence it was called rubber tetrabromide); that chlorine substitutes as well as adds, forming a so-called heptachloride[5] of the approximate formula $(C_{10}H_{13}Cl_7)_x$; and that the halogen acids form true addition products $(C_5H_9X)_x$.[6,7] Because of these additions, and those of sulfur and of sulfur monochloride,[8] S_2Cl_2, together with the studies of the oxidation of rubber, and especially because of Harries' work on the action of ozone,[9] there has finally developed a more complete theory of the structure of the rubber hydrocarbon, and proved by refractive index measurements,[10,11] chemists now believe it consists of many C_5H_8 groups with only one double bond in each group.[12] These polymerized groups are aggregated into larger masses, which show a diminished chemical activity. The structural formula may thus be written  $(-CH_2-C=\overset{\overset{CH_3}{|}}{C}H-CH_2-)_x$; but whether it is a long chain or a large ring is not known. The future has to do with the *x;* for precisely the way in which these groups of carbon and hydrogen are united to form the aggregates, and the effect on physical properties of the size of these aggregates, is one of the unsolved chemical problems in this intricate phase of organic chemistry.

During these past twenty-five years occurred what one of our well-known chemists, who has been so forceful in humanizing chemical knowledge, called "the race for rubber." Stimulated by the high price of natural rubber in 1910, the chemist assiduously pursued the chemical synthesis of the rubber hydrocarbon. From several starting points, he succeeded finally in developing a structure and a rubbery substance which upon analysis proved to be a true rubber. These syntheses were successful from a chemical standpoint, but they were not so in practice. Synthetic rubber, although vulcanized into numerous rubber products, never has had the final touch given to it which Nature adds in the tree. The products made from it had neither the life nor the strength possessed by those made from natural rubber. Although there was a race for rubber, the best that can be said for the chemist is that he ran on a different track than did the planters in the Far East, and arrived at a lesser goal.

Some of the admirable work which has been done in the adding of hydrogen to rubber,[13,14] or the various products made in the oxidation of rubber must be passed over with the statement that by the action of oxygen[15] on rubber several products are claimed to have been isolated, but few of them are pure materials and much is yet to be done. We know of the nitrosite[16] products, and of methyl and ethyl hydro rubber,[17] which latter are prepared through very difficult reactions with zinc methyl and zinc ethyl. A recent most interesting development of a theoretical nature has been the preparation of crystalline rubber.[18] Certain European chemists have recently found it possible to obtain actual crystals of rubber hydrocarbon from certain highly purified solutions. We have conceived of rubber as a colloidal plastic; and yet now the chemist has changed our colloid into crystals. The crystals are quite different from rubber as we know it. They are very sensitive to oxidation, and possess relatively little elasticity.

Vulcanization with Sulfur

From the practical standpoint, the vulcanization of rubber, or its combination with sulfur, is the field that has commanded the chief interest. Most of our commercial rubber products demand the interaction of rubber and sulfur, under the influence of temperature and time. These are the factors discovered by Goodyear in 1839, and they persist. Down to 1900 they were still much in the form left them by Goodyear. But from 1900 on, the energetic work of a number of

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[1] Received March 16, 1925. Presented before the Division of Industrial and Engineering Chemistry at the 69th Meeting of the American Chemical Society, Baltimore, Md., April 6 to 10, 1925.

[2] Vice president of The B. F. Goodrich Company.

[*] Numbers in text refer to bibliography at end of article.

chemists has led to the improvement, not only in our knowledge of what is vulcanization, but also in changes in the methods by which vulcanization can be carried out. The disputes between the advocates of a chemical addition theory of vulcanization and a physical adsorption theory are well known in rubber literature.

Vulcanization is concerned not only with sulfur and its effect on the rubber hydrocarbon, but also with the substance sulfur monochloride, the action of which was discovered in 1846 by Parkes[19] in Great Britain. The light shed upon the way sulfur acts is assisted by our knowledge of the changes brought about by halogens, oxygen, etc. Vulcanization is difficult of explanation because even with a given quantity of sulfur we are disturbed in our theories by variations in the finished product. The rubber man deals in "undercure," "overcure," and "proper cure." Did we deal with one unvaried material, with a constant percentage of sulfur, our problem would be simple.

We can, however, in the light of our knowledge undertake a few positive statements. There is, during vulcanization, a chemical reaction between rubber and sulfur, and during this reaction the rubber combines with some sulfur. We know that time and temperature[20] for a given mixing are factors; we know that when a mixture of rubber and sulfur is heated, the rubber dissolves the sulfur[21,22,23] and chemical action follows; and during this heating process we believe that the rubber aggregates are being broken down by the action of heat, so that the longer the time of heating, the relatively weaker is the product. These two actions go on simultaneously: the addition of sulfur and the breaking down of the rubber aggregate. Thus, in the simplest and shortest explanation that can be made, our theories lead us to believe that, whatever other effect may occur, there is at least a definite chemical action taking place during vulcanization, with heat and sulfur playing the major parts.

Accelerators

From a practical standpoint, next to the discovery of the effect of sulfur, the greatest advancement from chemical work has come from the use of those substances that speed the time and lower the temperature at which sulfur is added to rubber. These substances, broadly speaking, we term "accelerators of vulcanization." The use of such inorganic powders as white lead, litharge, and so on, was known to Goodyear and his contemporaries, but down to 1906 essentially nothing was done in the use of organic substances.

The story of the history of organic accelerators has been given in another place,[24,24a] and only a brief comment will be repeated here. It was one of our American chemists who found in 1906 that aniline oil and other nitrogenous organic chemicals, when added to mixtures of rubber and sulfur, shortened the time of vulcanization, and gave to the finished mixture higher physical values. The list of these organic compositions is long. Chemists have studied the effect of literally thousands of organic compositions used not only to accelerate vulcanization, but to yield better products. Among the inorganic accelerators, the chief ones of value are litharge, magnesium oxide, and zinc oxide, the latter being in point of fact used as a promoter of the organic accelerator. A large number of groups of accelerators are used, the effect of which upon the temperature of vulcanization is so varied that today it is possible to add sulfur to rubber and thus vulcanize it at temperatures ranging from slightly above that of the room up to temperatures which radically affect the aggregation of the rubber hydrocarbon.

The most important question worthy of discussion in this place is—just what is done by the accelerator? Let me state what is probably the most generally accepted theory; the one, at least, which is most plausible. The original proposer called it the hydrogen sulfide-polysulfide theory.[25] It consists simply (or rather complexly) in the belief that when amines are used as accelerators, hydrogen sulfide is formed and adds to itself sulfur to form a polysulfide in a manner analogous to the formation of ammonium sulfide. This polysulfide sulfur easily splits off a very active form of sulfur, which then quickly attaches itself to the rubber. The accelerator therefore serves to activate the quantity of sulfur in contact with rubber.

Our rubber factories are dominated by accelerators, and it is no idle statement to say that the practical results obtained by the chemist in the rubber industry have modified the handling of factories in a marked way. It is an achievement brought about during the last twenty-five years. The manufacturer on his part "turns over" his plant more rapidly, and has needed a smaller investment in order to meet the demands of the consumer of tires and other rubber goods than would have been required had there been none of this chemical work. The consumer, likewise, has profited by increased values. Part, although not all, of the well-recognized additional tire service is due to the qualities made possible by these organic accelerators during rubber vulcanization.

In connection with our story of vulcanization is another and more recent development, for chemists have found the role that is played by organic acids, the use of which is old in practice. One of our prominent chemists has analyzed natural rubber and found in it the presence of organic acids—oleic, linoleic, and one hitherto unknown which he calls "heveic" acid.[26] These acids have a definite influence on rubber vulcanization, since without their presence metallic oxides would fail as accelerators. Certain grades of rubber seem to be deficient in these acids; and this deficient rubber may be improved by the addition of organic acids in the presence of metallic oxides.

Rubber Latex

Mother Nature produces rubber in the form of little drops of rubber hydrocarbon and puts them into suspension in water in the glands of the rubber tree. This colloidal suspension, or latex as it is called, has been subject during the past ten years to a study of an intense character, and with many admirable additions to our knowledge.

To one interested in a further study of latex, its composition and properties, and the recent work in its industrial applications, no better reference can be made than to that most admirable paper (which to the writer is a classic in presentation) by van Rossem.[27]

Rubber latex is one of the most interesting of the colloidal suspensions. The globules of the rubber hydrocarbon are of various sizes and shapes—globular, pear-shaped, etc., varying in size from as low as 0.5μ in diameter to as high as 3.0μ. One recent investigator[28] succeeded in pricking some of these particles, and came to the conclusion that each particle is surrounded by an adsorbed layer of nonrubber substance, and each particle consists of two different rubber phases; one, the outer layer, which is scarcely soluble in benzene and of very high viscosity, and an inside fluid phase of low viscosity and soluble in benzene. The Brownian movement of these particles in the latex has been observed, and through cataphoresis experiments the rubber particles can be shown to have a negative charge.

Much work has been done on the practical methods of coagulation of latex, and studies of the properties of the rubber obtained by the use of various acids, salts, etc., as coagulants.

There seems to be no doubt that the protective colloid[29] in this suspension consists of proteins of an amphoteric character; and that the resin acids and soaps are constituents of the protective layer. Our acceptance of the latex as a colloidal system leads us to understand the coagulation process, but there still seems to be some difference of opinion among those who have studied it most closely regarding precisely the part played by enzymes and bacteria, and therefore exactly what happens when acids are added. We do generally agree, though, that coagulation results in a massing of the particles, and that the solid, dry, crude rubber as we get it consists of particles each surrounded by some proportion of the protective colloid originally in the latex.

During the past two years particularly, there has been considerable agitation in the industrial field over the application of latex in the rubber industry. Latex has been mixed with sulfur and powders and dried;[30] latex has been sprayed[31] as a means of obtaining dry rubber; it has been used to impregnate tire fabrics;[32] it has been used in making dipped goods; latex has been vulcanized without coagulation,[33] and the resulting vulcanized latex evaporated to form layers upon cloth, sheets of rubber, and other articles. With some degree of success latex has been used in the paper industry.[34] It is possible to ship latex from the Far East without coagulation by the use of preservatives;[35] it is possible to concentrate latex from the natural percentage of approximately 35 per cent total solids up to 60 per cent, and even 75 per cent.[36,37] The creation of an artificial latex or rubber suspension by mechanical means from solid, dry rubber has been carried out.[38]

From the practical manufacturing standpoint, none of these new processes in the direct application of latex has extended into the industry in any large way. Many of the scientists and some of the technologists seem to believe that the uses of latex industrially have but just begun, and do not represent a mere temporary enthusiasm.

Colloid Chemistry of Rubber Cements

The vulcanization of rubber in sol and gel form has attracted the attention of some clever chemists, who have succeeded in vulcanizing rubber solutions in benzene without the formation of a gel,[39-43] and subsequently evaporating to a film of vulcanized rubber. They have also vulcanized such solutions to true gels. This has led some chemists to speculate on the colloid chemical nature of vulcanized rubber, and some of them seem to believe that when the evidence is all in, vulcanized rubber will be found to be a gel consisting of a chemical addition product of sulfur and rubber, in the presence of rubber or some physically changed modification.[44,44a]

Colloid Chemistry of Rubber Mixtures

In the old days dry powders were added to soft rubber mixtures for the sake of making them stiffer than was possible with sulfur alone, and for cheapening purposes. They were called "fillers." Today the rubber mixture is considered by the rubber chemist as a disperse system of a very particular character,[45] and each of these dry powders which we now know as "pigments" in any such system is used to obtain defined values. In studies that have been published, two characteristics of great value are shown in such systems. The fineness of subdivision, or, as we now call it, "particle size," is of prime importance; for particle size affects not only the property of stiffness of the dispersion but also such important characteristics as resistance to abrasion, tensile strength, the modulus of elasticity, and so on.[46] Particle size alone, however, does not account for the valuable characteristics of some of these more modernly considered pigments such as carbon black and zinc oxide; and we today are looking toward the ultimate solution of the question in the evaluation in terms of physical constants of the interfacial tension between the rubber and the surface of these particles.[47,48]

There is doubtless still another important characteristic in the shape of the particles. It may be a question of total surface which today is not possible of evaluation with our present microscopic methods; but it is true that certain carbon blacks—for instance, the particle size of which is in the order of certain other blacks—yield, when vulcanized in rubber, softer mixtures; yet others of nearly equally fine subdivision yield stiffer mixtures. So we must consider not only particle size but also the unmeasured interfacial tension constants and the degree of plasticity shown by given volumes of given substances.

There is a science as well as an art in modern rubber compounding, and while this phase of rubber chemistry is passed over rapidly, this is done largely, not from lack of exact data, for in point of fact it is the rubber mixture that constitutes the rubber business, but from the lack of coördinated conclusions. Mixtures are made to have different properties for each of many thousand different uses. The future rather than the past holds the key to the evaluation and predetermination of characteristics to be given to finished mixtures because of known physical and chemical characteristics possessed by substances to be dispersed into the rubber phase.

Many other of our problems might be mentioned for which some solution or theories have been offered, such as that of mastication and the effect of it upon the protective colloid; the effect of heat prior to vulcanization; the effect of acids and alkalies upon rubber; but these numerous subjects must be passed over at this time.

Aging of Rubber

In the old days a rubber mixture after vulcanization was not expected to last, on ordinary standing, in the light, or at ordinary temperatures, for more than one or two years; it became hard and evil-smelling. Chemists, however, separated certain products, resinous in character, from this so-called "deteriorated" rubber. It has ever been a study on the part of chemists to determine what to do to prevent this deterioration through aging, and how to test in advance whether any given composition after any given cure would live out a long enough useful life. The question, therefore, in front of the manufacturer has been—how long will it last?

Within the last twenty-five years various methods for testing this aging, and various apparatus for working out accelerated aging tests, have become known and used.[49,50] Apparently, there is no unanimous view as to which particular method of test is superior, but the majority of rubber manufacturing laboratories today use one test or another for this purpose.

In the study of aging more light has been thrown upon the precise chemical mechanism of it. It is generaly conceded at the present day that aging has to do with oxidation. Whether it is direct oxidation of the rubber or whether it is an oxidation of the free sulfur, and from those oxidation products a catalytic action is developed, chemists do not seem wholly to agree.[15,51,52,53] Oxidation products of rubber, however, have been collected when rubber has been submitted in closed vessels to the action of air at ordinary as well as at elevated temperatures. To prevent this oxidation a number of substances have been used.[54,55] These as a rule have been nonaccelerators of vulcanization, but they do serve to retard the action of oxygen. We are not, however, quite ready to state whether they serve as buffers to take oxygen instead of the rubber taking it, or whether they serve definitely to reduce the ability of rubber to add oxygen. There is still much opportunity for study in the question of aging. But our modern rubber mixtures do last over a reasonable period of years.

Vulcanization without Sulfur

Since sulfur seemed to be *the* substance which gave to rubber improved properties by vulcanization, it is natural that many chemists should have studied the problem of vulcanization *without* sulfur.[56,57,58] Several substances, notably certain peroxides and certain aromatic nitro compounds,[59,60] have been found definitely to bring about a stiffening, an increase in strength, and the other physical changes that we call results of vulcanization. None of these, however, so far as the published literature goes, are known to give properties that equal, let alone be superior to, the products obtained from the use of sulfur. They are, therefore, pretty largely only of scientific interest.

Psychology of Rubber Chemistry

It would not be in keeping with this review were no comment made upon the changed attitude, during the past twenty-five years, on the part of rubber manufacturing companies, so far as secrecy is concerned. Rubber factories were formerly closed to visitors. Nowadays we have found the advantages to be gained through somewhat full and free discussion of our technical affairs.

Significant in this change of attitude on the part of the directors of industrial rubber companies has been the growth of the Rubber Division of the AMERICAN CHEMICAL SOCIETY. It was born in Boston as a section in 1909, authorized as a division in 1919, and has been animated by commendable enthusiasm. Particularly significant, since the city of Akron, Ohio, is the rubber center of the world, was the organization of the Akron Section of the AMERICAN CHEMICAL SOCIETY in 1923. Rubber chemists in Akron meet together freely, and although it is admitted that for broadening purposes we customarily discuss topics other than rubber in our Akron meetings, yet in the Rubber Division of this SOCIETY papers have been numerous upon subjects which twenty-five years ago would have caused hands of superintendents and directors to be raised in holy horror.

We have come to the conclusion that "we live in deeds, not years," and an atmosphere of friendly competition and good sportsmanship now envelops the rubber industry.

Bibliography

1—Faraday, *Mag. Pharm.*, **14**, 180 (1826): Analyzed rubber distillate.

2—Williams, *Trans. Roy. Soc. London*, 241 (1860): Characterized isoprene.

3—Gladstone and Hibbert, *J. Chem. Soc.* (*London*), **53**, 679 (1888): Optical measurements.

4—Weber, *Gummi-Ztg.*, **16**, 527, 545, 559, 561 (1902): Action of S on rubber.

4*a*—Weber, *Ber.*, **33**, 779 (1900).

5—Peachey, English Patent 1894 (1915) (cf. References 3 and 7): Heptachloride.

6—Harries, *Ber.*, **46**, 733 (1913): Addition of halogen acids.

7—Hinrichsen, Quensell, and Kindscher, *Ibid.*, **46**, 1283 (1913): Addition of halogen acids.

8—Weber, *J. Soc. Chem. Ind.*, **13**, 11 (1894): Addition of sulfur chloride; cf. Hinrichsen and Kindscher, *Ber.*, **46**, 1291 (1913); *Kolloid-Z.*, **6**, 202 (1910); Bernstein, *Ibid.*, **11**, 185 (1912).

9—Harries, *Ber.*, **37**, 2708 (1904); **38**, 1195, 3985 (1905); **45**, 936, 943 (1912): Ozone reaction.

10—Macallum and Whitby, *Trans. Roy. Soc. Can.*, **18**, 191 (1924): Refractive index.

11—Twiss, *Nature*, **113**, 822 (1924): Refractive index.

12—Harries, *Ann.*, **406**, 173 (1914): Rubber as aggregate of C_5H_8 groups.

13—Pummerer and Burkard, *Ber.*, **55**, 3458 (1922); Pummerer and Koch, *Ann.*, **438**, 294 (1924): Hydrogenation.

14—Staudinger and Fritschi, *Helvetica Chim. Acta*, **5**, 785 (1922): Hydrogenation.

15—Herbst, *Ber.*, **39**, 523 (1906); Kirchhof, *Kolloid-Z.*, **13**, 40 (1916); Peachey, *India Rubber J.*, **45**, 361 (1913); cf. Fisher, *Ind. Eng. Chem.*, **16**, 627 (1924): Addition of oxygen.

16—Harries, *Ber.*, **34**, 2991 (1901); **35**, 3256, 4429 (1902); **36**, 1937 (1903): Nitrosites.

17—Staudinger and Widmer, *Helvetica Chim. Acta*, **7**, 842 (1924): Methyl and ethyl hydro-rubber.

18—Pummerer and Koch, *Ann.*, **438**, 294 (1924): Crystalline rubber.

19—Parkes, English Patent 11,147 (1846): Sulfur chloride cure.

20—Weber, *Kolloid-Z.*, **1**, 33, 65 (1906): Time and temperature factors.

21—Hinrichsen, *Ibid.*, **8**, 245 (1911): Rubber dissolves S, then reacts.

22—Venable and Green, *Ind. Eng. Chem.*, **14**, 319 (1922): Solubility of S in rubber.

23—Kelly and Ayers, *Ibid.*, **16**, 148 (1924): Solubility of S in rubber.

24—Geer, *Ibid.*, **14**, 369 (1922): History of accelerators.

24*a*—Geer and Bedford, *Ibid.*, **17**, 393 (1925).

25—Bedford and Scott, *Ibid.*, **12**, 31 (1920); **13**, 125 (1921); cf. Sebrell, "Organic Accelerators of Vulcanization," in Bedford and Winkelmann's "Systematic Survey of Rubber Chemistry:" Polysulfide theory.

26—Whitby and Dolid, *India Rubber World*, **68**, 496 (1923); Whitby, *Brit. Assoc. Adv. Sci., Rept.*, **1923**, 432; *India Rubber J.*, **68**, 617, 735 (1924): Fatty acids in rubber.

27—Van Rossem, *Rubber Age* (*London*), **5**, 523 (1924); *J. Soc. Chem. Ind.*, **44**, 33T (1925): Latex.

28—Hauser, *India Rubber J.*, **68**, 19, 725 (1924); Freundlich and Hauser, *Kolloid-Z.*, **36**, (Zsigmondy-Festschrift), 15 (1925): Microscopy of latex.

29—Belgrave, *Malayan Agr. J.*, **11**, 348 (1923): Protective colloid in latex.

30—Laub, *Bull. Rubber Growers' Assoc.*, **4**, 209, 321 (1922): Latex S fillers.

31—Hopkinson, U. S. Patent 1,424,020 (1922): Sprayed latex.

32—Hopkinson, *Ind. Eng. Chem.*, **15**, 1267 (1923): Impregnating tire fabrics.

33—Schidrowitz, English Patent 193,451 (1921): Vulcanized latex.

34—Kaye, *Bull. Rubber Growers' Assoc.*, **4**, 408, 506 (1922): Latex paper.

35—De Vries, *Arch. Rubbercultuur*, **7**, 168 (1923): Preserved latex.

36—Gibbons and Shepard (General Rubber Co.), English Patent 218,544 (1924); McGavack (General Rubber Co.), U. S. Patent 1,523,821 (1925): Concentrated latex.

37—Hauser (K. D. P., Ltd.), English Patents 213,886 and 219,277 (1924): Concentrated latex.

38—Pratt, Italian Patent 225,949 (1923); *India Rubber World*, **69**, 785 (1924): Water dispersion.

39—Helbronner and Bernstein, *Rept. 4th Intern. Rubber Congress, London*, **1914**, p. 156: Vulcanization in solution.

40—Peachey, English Patent 129,826 (1919); 146,734 (1919); *India Rubber J.*, **59**, 1195 (1920): Vulcanization in solution.

41—Stevens, English Patent 164,770 (1920); *India Rubber J.*, **61**, 1160; **62**, 203 (1921): Vulcanization in solution.

42—Le Blanc and Kröger, *Z. Elektrochem.*, **27**, 335 (1921): Vulcanization in solution.

43—Boiry, *Caoutchouc gutta-percha*, **21**, 12,257, 12,293, 12,335, 12,386, 12,454 (1924); **22**, 12,507 (1925): Vulcanization in solution.

44—Ostromuislenskii, *J. Russ. Phys. Chem. Soc.*, **47**, 1453, 1462, 1467 (1915); *India Rubber J.*, **52**, 467 (1916): Theory of vulcanization.

44*a*—Twiss, *J. Soc. Chem. Ind.*, **44**, 106T (1925): Theory of vulcanization.

45—Green, *J. Ind. Eng. Chem.*, **13**, 130 (1921); *J. Franklin Inst.*, **192**, 637 (1921); *Chem. Met. Eng.*, **28**, 53 (1923): Rubber pigments.

46—Green, *J. Ind. Eng. Chem.*, **13**, 1029 (1921): Colloid chemistry of pigments.

47—Wiegand, *Can. Chem. J.*, **4**, 160 (1920); cf. Spear, Colloid Symposium Monograph (Madison), **1923**, p. 321: Colloidal pigments.

48—Klein and Parrish, *J. Oil Colour Chem. Assoc.*, **7**, 54, 82 (1924): Colloidal chemistry of rubber pigments.

49—Geer and Evans, *Rubber Age* (*London*), **2**, 308 (1921): Aging.

50—Bierer and Davis, *Ind. Eng. Chem.*, **16**, 711 (1924): Aging.

51—Peachey, *J. Soc. Chem. Ind.*, **31**, 1103 (1912); **32**, 179 (1913); **37**, 55 (1918): Oxidation.

52—Bruni, *India Rubber J.*, **63**, 415, 814 (1922): Oxidation.

53—Marzetti, *Giorn. chim. ind. appl.*, **5**, 122 (1923): Oxidation.

54—Moureu and Dufraisse, English Patent 181,365 (1922): Antioxidants.

55—Bayer & Co., D. R. P. 257,813; 264,820 (1911); 259,722 (1922); 329,676: Antioxidants.

56—Degen and Kuth, English Patent 9956 (1908): Iodine cure.

57—Klopstock, D. R. P. 260,916 (1912): Selenium, tellurium cures.

58—Boggs, *J. Ind. Eng. Chem.*, **10**, 117 (1918): Selenium cures.

59—Ostromuislenskii, *J. Russ. Phys. Chem. Soc.*, **47**, 1462, 1467, 1885, 1898, 1904 (1915); **48**, 1114 (1916); *Caoutchouc & gutta-percha*, **14**, 9119 (1917): Cures with active oxidizing agents.

60—Gibbons, U. S. Patent 1,291,828 (1919): Nitroanthraquinone cures.

Ten Years of Sugar Refining[1]

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TEN years ago, and even long before that, the process of refining raw cane sugar had already reached a highly perfected state; so much so that refined granulated sugar was at that time, as it is now, one of the most nearly chemically pure of all commodities. Neither were the principles involved in the refining process materially different from what they are today. The bulk of the raw sugar received consisted, as it does now, of high-grade centrifugals which were washed to a purity of approximately 99 degrees. The use of animal blood for clarification had long since been abandoned in favor of phosphoric acid compounds. The best refiners attached the same importance to perfect mechanical filtration as we now know to be essential for the production of white granulated sugar. Bone black was used for epuration in precisely the same manner as today, and was at least as effective in decolorizing and otherwise purifying the liquors; in fact, many refiners believe that the bone black manufactured up until a few years ago was of better quality and less friable, by reason of a more plenteous supply of bones suitable for its manufacture, than is the present-day product. The spinning, washing, and drying of refined sugars have not changed materially in principle. In methods and equipment, however, much important progress has been made. There have been considerable improvements in labor-saving and other cost-reducing devices.

Raw Sugar Washing

As to the affination process, the self-discharging centrifugal basket used in several modern installations has fully proved its value. By its means the number of operators required at the washing station is materially reduced and with careful control the quality of the washed sugar is quite as good as ever. The basket consists of a shell, the top portion of which is cylindrical in form, with a lower section narrowing in diameter to form an inverted, truncated cone open at the bottom. The magma to be spun drops on a horizontal disk mounted on the spindle within the basket and is thrown out against the side of the basket by centrifugal force. The angle formed by the conical section is steeper than the angle of repose of the load and, as the machine is braked, the charge falls through the open bottom. Direct motor drive has made it possible to bring modern machines to full speed in remarkably short time and improved brakes have greatly shortened the braking period. One 48-inch machine of the type described will handle a quarter of a million pounds of raw sugar in 24 hours. It is all important for perfect and efficient operation so to train the operators that they perform each step with the regularity of a pendulum. The proper cycle of operation must first be worked out by intelligent study for each installation and for varying amounts of melt. When this is once established and each man is assigned to the proper number of machines, it is only necessary for each to charge, wash, and brake his machines in rotation at a measured pace, neither hurried nor sluggish. Only by such regularity can uniformly good washing be maintained.

Much has been done in the development of washing devices for centrifugals. Most of these deliver a measured quantity of water when a lever is turned by hand and are refilled as the lever is reversed. Some distribute the water in a fanlike spray over the surface of the sugar, whereas others have an oscillating spray which directs a heavier stream of water progressively from top to bottom of the basket. Most centrifugals for both raw and refined sugar are now equipped with one or another of the many measuring devices and sprays.

One refinery has worked out an elaborate and ingenious system of automatic operation for its centrifugals by means of electrical control. In a battery of machines every operation except charging is electrically timed and operated. The writer saw in this plant one machine experimentally equipped which was even charged automatically, so that practically the only labor required for a battery of such was for supervision and maintenance.

Filtration

Leaf filters began to replace the old bag filters in 1914. Infusorial earth as a filter aid was substituted for compounds of phosphoric acid wherever leaf filters were installed. The latter are operated under high pressure and phosphate of lime does not form a sufficiently porous cake under these conditions. On account of the cost of infusorial earth, which largely balances the savings in labor and filter cloth, both large items for the old bag filters, the economy of leaf filters has been questioned by some refiners. In fact, so great has been the conservatism with respect to leaf filters, especially for the filtration of affination sirup, that not only have many existing bag installations been allowed to stand, but a new refinery has recently been equipped with bag filters. In the writer's opinion, however, there is no doubt of sufficient net saving in the combined items of labor, cloth, and filter aid, to render an installation of leaf filters, properly operated, a profitable investment. Furthermore, the cleanliness attending the operation of leaf filters, and the rapidity with which the liquors pass through the process, both factors reducing the liability of sucrose losses through inversion, are features not to be overlooked.

Devices for sluicing the leaf filters automatically have decreased the labor required at the filter station in several refineries. Rotary suction filters with continuous, automatic removal of the cake have replaced in some plants the usual types of filter presses for the filtration of sluicings from leaf filters.

An improved form of infusorial earth, prepared by a process in which calcination is understood to play a part, has been placed on the market within the last two years. This material at first gave a greatly increased liquor flow, but left something to be desired in clarity of filtrate. It has been the effort of the manufacturers so to modify the prepared earth as to give perfect filtration without sacrificing rate of flow, and the product now being turned out seems to give promise in that direction.

Regeneration of infusorial earth has been discussed ever since the material came into general use in connection with leaf type filters. Many laboratory and some plant scale experiments showed that the earth could be efficiently revivified by burning, but several years elapsed before regeneration was put into actual practice. One refinery is now burning earth in the form of cake from suction filters in rotary kilns; another has demonstrated the effectiveness of a station-

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ary kiln of the type used for burning lime, for calcining earth recovered as filter press cake. In both cases the earth must be reduced to a finely divided state, for which purpose wet grinding is preferred.

About three years ago the use of paper pulp as a filter aid was proposed. It was first tried in leaf filters of the rotary type, which has since proved to be the only type applicable to this form of filtration. Several attempts were made to adapt the stationary leaf filters to pulp filtration, but, so far as the author knows, the project has been abandoned. The pulp filter cake is extremely porous, is bulky, and must be quite evenly coated on the cloth. This is difficult to accomplish in any but the rotary type of filter. Removal of the cake is also accomplished more easily with the latter type. The used pulp is regenerated by merely washing out the impurities with hot water, for which purpose a form of washer common to the paper manufacturing industry is employed. A large quantity of water is required, but since waste water from the washing of char filters can be used the expense is small. Paper pulp is furnished by the manufacturers in the form of thick sheets. Soda pulp, or a mixture of same with ground wood, is generally used, though it is said that old newspapers work equally well. New pulp is fed to the beater, a device also known to the paper industry, where it is beaten to a thick cream with sufficient water. The make-up of new pulp required is said to be surprisingly small, since mechanical loss through the washing screens is not great and the quality of the pulp does not appear to suffer after repeated use. Pulp filtration is characterized by a high rate of flow.

There still exists, however, a difference of opinion as to whether sufficiently clear liquors can be obtained at all times in refinery practice. It was early found that double or triple filtration through a heavy coating of pulp is necessary, and that the pulp must be augmented with a small proportion of some coagulant, such as phosphoric acid. This decreases the rate of flow, which remains, however, still relatively great.

In the case of filtration with infusorial earth, if a trace of the filter aid passes into the filtered liquor, because of broken cloths or otherwise, it is caught in the char filters. In pulp filtration, on the other hand, if the filtrate is ever so slightly contaminated, it is sure to appear hazy after char filtration, and the fine suspended or colloidal matter persists and becomes more concentrated in the granulated sirups, to the detriment of the refined product. It is therefore essential in pulp filtration to obtain highly brilliant filtrates, and apparently all refiners who have tried it have not met with the same degree of success in the accomplishment.

Bone black filtration presents little that is new. The continuous system of filtration has almost entirely replaced the old battery method, however, in line with the tendency of the times to cut down to the absolute minimum the amount of material carried in process. Oil firing of the kilns has become more widely used. A retort made in two sections is expected to cut renewal costs, since either top or bottom section can be replaced, separately, and the scrapping of the entire retort thus avoided.

Evaporation

In the pan house a notable innovation has been the installation of multiple-effect evaporators for concentrating liquors previous to entering the pans. Sugar boilers have been able to accommodate themselves to handling pan liquors at 68° Brix, so that if the liquor runs from the bone black filters at 55° Brix it is possible to accomplish about one-half the total evaporation in multiple effect, and largely with exhaust steam. The saving effected is, of course, very great. Another medium for the utilization of exhaust steam for evaporation is the calandria pan. Widely used in the raw cane sugar factories of Cuba, it has been adopted in some of our modern refineries.

Refined-Sugar Machines

Improvements in centrifugal machines have been discussed in connection with raw sugar washing. Although it has not been possible to apply the self-discharging principle to refined sugar machines, direct motor drive and various mechanical improvements have greatly increased their efficiency and eliminated labor. Separation of wash sirups from greens is now pretty generally applied to the lower granulated and remelt sirups.

Drying and Screening

Methods of drying and screening sugar have remained practically unchanged during the last decade, except for the introduction to a very limited extent of air drying for the coarse-grained sugars to improve their brilliance. This has been accomplished by spreading sugar from the centrifugals in a thin layer on a slow moving belt, or, as in one case that has come to the writer's notice, by leading a current of warm, dry air through the housings of the screens used for sizing. At least in the former method it is essential to heat the sugar first by introducing steam into the centrifugal basket.

Packing and Other Handling

The packaging of sugar has received a liberal share of attention and some wonderfully ingenious devices have been perfected in this field of endeavor. Automatic feeders for the carton-filling machines, container-sealing machines, bag-filling equipment, and a variety of ingenious arrangements for filling cartons of soft sugar and for the tight packing of tablets and cubes are but a few of the many interesting improvements.

Methods of conveying, elevating, pumping, trucking, and otherwise handling the enormous quantity of material that daily passes through a modern refinery have kept pace with the engineering progress of the times, as have also the means of generating the prodigious quantities of steam and electric power required.

Progress in the Laboratory

Last but not least, our chemical laboratories, guardians of the refining process and insurers of quality in the product, have kept in the vanguard of progress. Control of the refining process is being assisted by modern methods of hydrogen-ion determination and by systematic color readings according to one or another method for expressing color as a numerical value. Screen analysis has been placed on a scientific basis. Apparatus has been devised for comparing the filtrability of raw sugars and the efficiency of different filter aids, so that these variables can now be expressed in figures. Routine purity determinations have been shortened by improved methods and equipment.

The sugar refining industry is, by the very nature of the vast scale of its operations, a conservative industry. A change in method usually means a change in equipment, and, since most of the equipment is large and costly, a considerable outlay of money is generally involved. The foregoing summary of a decade's progress, however, will indicate that the industry's technical progress is steady and material, even though along conservative lines.

An investigation which is being conducted by the Bureau of Mines to determine possible improvements in the milling of fluorspar indicates that considerable improvement in concentration and more economical recovery may be effected.

Prevention of Evaporation Losses from Gasoline Storage Tanks[1]

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The loss of gasoline from storage tanks with roofs tight enough to keep out the wind is due almost entirely to the daily breathing out of gasoline-saturated air as the temperature increases. Various methods for preventing this evaporation loss have been tried, but the most satisfactory means of saving the exhaled vapors seems to be the breather bags developed by this laboratory in 1923.

Careful weekly gagings made from March to November, 1924, show that these bags reduced the average monthly evaporation loss during this entire period from 0.25 to 0.04 per cent of the tank contents, or a saving of 6900 gallons per tank per month. Strength and other tests on balloons and fabric in use for 22 months show no appreciable deterioration. The average life of the balloons will certainly not be under four years in this climate, and a much longer life seems quite probable.

Cost data and suggestions for other possible applications of these breather bags are given.

The serious magnitude of the loss by evaporation of petroleum fractions during storage and handling was first investigated quantitatively by Wiggins,[2] who showed that the lightest and most valuable fractions of crude oil to the extent of 6 or 7 per cent are commonly lost by evaporation between the well and the refinery. Later reports by Wiggins[3] and Schmidt[4] point out various methods for reducing these losses. Other investigators,[5] interested in some particular device for preventing evaporation, have also gathered valuable data, confirming the conclusions of Wiggins. Most of this work has been done on crude oil, although Schmidt studied the evaporation of gasoline from 250- and 500-barrel storage tanks. However, since it is the gasoline fraction that evaporates from crude oil, an even greater rate of loss would be expected in the refinery storage of finished gasoline.

For two seasons this laboratory has been studying the losses from eleven 120 × 40 foot gasoline storage tanks (holding about 67,000 50-gallon barrels) at the Whiting refinery, trying out a number of new devices for reducing these losses. The best of these appears to be the so-called "breather bag" or "balloon," a new and surprisingly effective means of stopping the breathing loss. This paper deals with the development of the breather bags and the results of their application to several gasoline storage tanks.

Breathing of Storage Tanks

The vapor in an average storage tank is at practically constant temperature every night for several hours just preceding sunrise, during which time equilibrium is substantially reached between the liquid gasoline and the vapor. As the temperature of the vapor rises during the daytime the saturated mixture expands, part of it being displaced through the vent or breather pipe. At the same time the temperature and vapor pressure of the surface layer of gasoline rise rather rapidly, causing a further evaporation thereof, and a corresponding displacement of the overlying vapor will take place in addition to the displacement due to simple thermal expansion. Most of the previous investigators of the subject have entirely overlooked the latter cause of breathing, which is really the largest factor, and have calculated that the volume of gas expelled by thermal expansion is comparatively small and could scarcely account for the observed losses.

As the vapor and oil surface cool off during the afternoon and evening this process is reversed, gasoline vapor being condensed into the liquid and the whole vapor volume shrinking as its temperature falls. To maintain atmospheric pressure within the tank, fresh air is sucked in from outside and is saturated with gasoline vapor before morning. This periodic exhaling of mixed vapors and inhaling of fresh air due to temperature fluctuations is known as breathing.

The loss of gasoline due to such breathing can be calculated only by making numerous assumptions as indicated in the following example. This calculation is based on temperature changes which have been found typical of an *average* clear summer day at Whiting. The loss is figured per 1000 cubic feet of vapor space so that it can be applied to any tank containing the same kind of oil and undergoing the same temperature change. A constant barometric pressure of 750 mm. of mercury is assumed. Figure 1 is the vapor pressure curve for Red Crown gasoline, determined by the method of Tizzard and Marshall,[6] which is used for this calculation.

Note—It will be noted that this curve indicates a boiling point (vapor pressure of 760 mm.) of 137° F., whereas a regular A.S.T.M. distillation test gives a figure of about 100° F. This is determined, however, with the thermometer in the vapor, and really measures the temperature of condensation of the lightest ends in the gasoline. If another thermometer is placed in the liquid at the same time it shows a true boiling point in the ordinary sense 30 to 60 degrees higher than that indicated by the thermometer in the vapor.

Assuming that at night the surface temperature of the gasoline and the vapor above it reach equilibrium at 75° F., where the gasoline has a vapor pressure of 265 mm., then the pounds of air per 1000 cubic feet of vapor mixture will be:

$$\text{Air} = 1000 \times \frac{29^*}{359} \times \frac{750-265}{750} \times \frac{750}{760} \times \frac{492}{535} = 47.4 \text{ pounds}$$

* Remembering that the molecular weight of a gas in pounds always occupies substantially 359 cubic feet under standard conditions.

At the hottest part of the day the maximum vapor temperature is assumed to be 105° F. (much hotter than outside air

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[1] Received July 9, 1925. Presented before the Joint Meeting of the Division of Petroleum Chemistry and Division of Gas and Fuel Chemistry at the 70th Meeting of the American Chemical Society, Los Angeles, Calif., August 3 to 8, 1925.

[2] *Bur. Mines, Bull.* **200** (1922).

[3] *Ibid., Tech. Paper* **319** (1923).

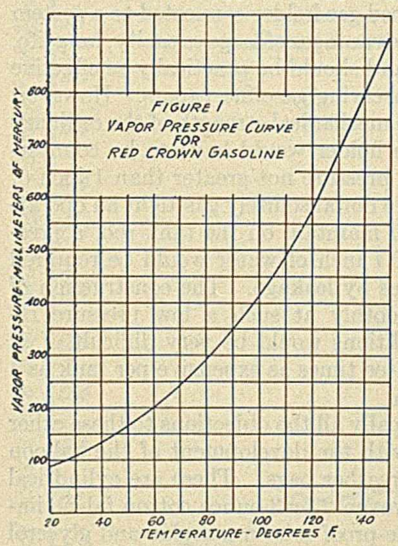
[4] *Ibid., Repts. Investigations* **2531** (1923).

[5] Johns-Manville Co., Catalog: "J-M Vapor Tight Insulated Tank Top," **1923.**

[6] *J. Inst. Petroleum Tech.*, **8**, 217 (1922).

due to radiation from the sun) and the concentration of gasoline in the vapor to be in equilibrium with the surface of the gasoline, the temperature of which is 95° F. The weight of air in the vapor mixture at this time would be:

$$\text{Air} = 1000 \times \frac{750-375}{750} \times \frac{750}{760} \times \frac{492}{565} \times \frac{29}{359} = 34.7 \text{ pounds}$$



Under these conditions the weight of air breathed out would be 47.4 − 34.7 = 12.7 pounds per 1000 cubic feet of vapor space. Assuming that the average temperature and the partial pressure of gasoline in the expelled air was the mean between the initial and final states in these respects, the volume of air and gasoline breathed out is calculated as follows:

$$\text{Volume of air at 750 mm. pressure} = 12.7 \times \frac{359}{29} \times \frac{550}{492} \times \frac{760}{750} = 178 \text{ cubic feet}$$

$$\text{Volume of gasoline vapor} = 178 \times \frac{320}{750-320} = 132.5 \text{ cubic feet}$$

$$\text{Total volume breathed out} = 310 \text{ cubic feet}$$

A 120 × 40 foot storage tank with an 8-foot pitch to the roof filled to the 39-foot level has a vapor space of 41,500 cubic feet for which the above daily breathing loss would be 12,900 cubic feet. If the average composition of the hydrocarbons in the vapor is assumed to be hexane, the volume of liquid hexane lost per breath is as follows:

$$132.5 \times 41.5 \times \frac{492}{550} \times \frac{750}{760} \times 0.24 = 1165 \text{ pounds or } 215 \text{ gallons}$$

By filling these tanks to 39.5 feet the vapor space is reduced to 35,800 cubic feet and the volume breathed would be 11,100 cubic feet. Assuming the richness of the vapor to be the same as before, the gasoline loss would be only about 86 per cent of its former value.

Although these calculated volumes breathed are somewhat higher, and the calculated gasoline losses somewhat smaller, than those actually measured, they are of the right order of magnitude, and illustrate the relative importance of the different factors.

If the rise in vapor temperature from 75° to 105° F. had been unaccompanied by evaporation of more gasoline, as some investigators have assumed, the breath due to simple expansion would have amounted to only 55 cubic feet per 1000 cubic feet of vapor space. Of this, $\frac{265}{750} \times 55$, or 19.5 cubic feet, would have been gasoline vapor, which is only 14.7 per cent of the calculated loss when the displacement of the air by the increased vapor pressure of gasoline is taken into account.

Siphoning—The measured loss figures on many tanks were considerably higher than the foregoing calculations would indicate. In searching for an explanation of this discrepancy it was discovered that on many tanks gasoline vapors continue to pour from the end of a breather pipe which comes down near the ground, even after the temperature in the vapor space of the tank has stopped rising. This effect, at first quite surprising, is due to the siphoning of the heavy hydrocarbon vapors from the higher to the lower level.

The continuance of this action is made possible by sucking air through the minute leaks which generally exist even in fairly good tank roofs (and possibly by an upward flowing current of air through the top section of the breather pipe). Measurements during 1923 showed that this siphoning action might cause the loss from a given tank to be 0.1 per cent per month higher than it would otherwise be. To check this siphon action, various types of liquid seals have been used and all breather bags are loaded so they will not start to fill until the gas pressure at the bottom of the breather pipe exceeds the siphon head of about 0.2 inch of water.

Methods of Reducing Breathing Losses

Regardless of the numerical accuracy of the foregoing calculations of breathing losses, they do point out the savings resulting from a small vapor space above the gasoline, and from the reduction to a minimum of temperature changes in vapor space and oil surface. A brief discussion of the available methods for accomplishing these results follows.

Reduction of Vapor Space—To reduce the vapor space in existing tankage the only feasible procedure is to maintain the gasoline at the highest level safety will permit. New tankage should be built with the lowest possible pitch to the roofs, to reduce the vapor space still further. Floating roofs reduce the vapor space to practically zero and are well worth considering on new construction of small working tanks. They are, however, very expensive to apply to existing tankage. On large storage tanks there is likely to be considerable mechanical difficulty, especially in climates where snow and ice is a factor. The scraping action of the shoe against the tank wall tends to produce dirt, accelerate corrosion, and possibly strike a spark.

The floating foam Sealite also reduces the vapor space to zero, but can only be used on oil in storage. Here it must in general be renewed at a cost of over $3000 per 120-foot tank every time a tank is emptied and often gives trouble by getting mixed with the oil as it is pumped out. In humid climates Sealite tends to absorb water, which sometimes causes the foam to break and sink through the oil.

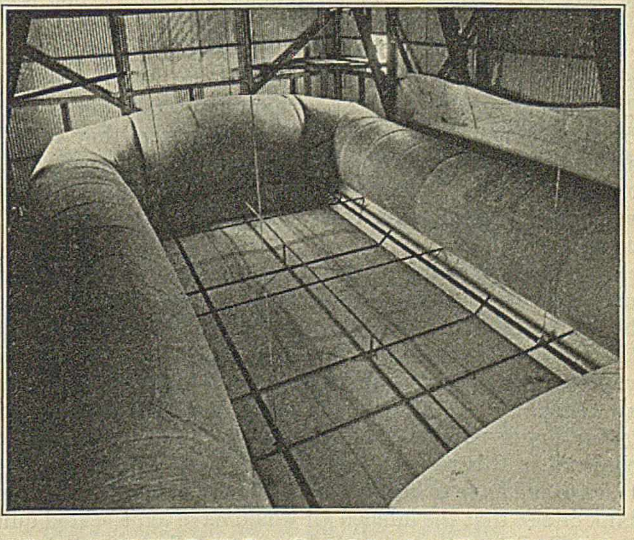
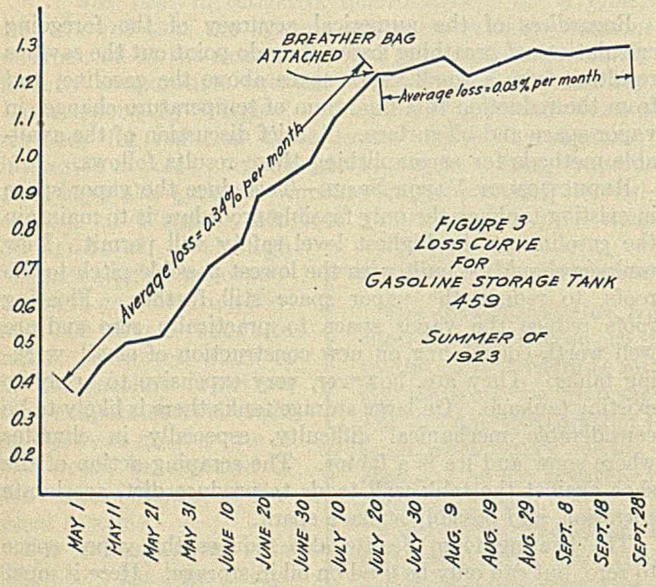


Figure 2—18,000-Cubic Foot Container about Two-Thirds Full, Viewed from Above, Showing Balloon Weight and One Counterweight Belt

Reduction of Temperature Variations—Having an irreducible vapor space which must of necessity be filled with air saturated with gasoline and must undergo daily temperature changes, the temperature range can be reduced by any of numerous methods. The methods that have been most successful in practice are (1) insulation with hair, felt, or cork, (2) shielding with a false roof, (3) painting with a highly reflecting aluminium paint, and (4) spraying with water during the period of naturally rising temperature. Although the first of these methods will save about 65 per cent of the normal loss, none of them effect nearly so complete a saving of gasoline as the breather bag, and the first two cost more than a breather bag installation. The third is cheaper but less efficient at the start and becomes almost ineffective after a few months' exposure to the average refinery atmosphere. The fourth requires constant attention to keep the lines and nozzles clean and usually necessitates yearly repainting of the tank.



Conservation of Vapors Breathed—All the devices for reducing breathing mentioned above, with the exception of the floating roof and Sealite, still permit a very considerable loss by evaporation. Hence there is a great opportunity for some method of preventing the loss of any exhaled vapors or recovering their gasoline content whether or not their volume has been reduced by other protective measures.

Absorption Plants. Gathering systems connected with a central absorption plant are effective but very expensive. They are especially unsuited for gasoline storage tanks, since by maintaining a slight vacuum on the system they suck in air through small leaks and thus accelerate rather than retard the evaporation. The recovered light ends cannot be conveniently blended again with the gasoline from which they came.

Another suggestion by one of the writers[7] was that individual absorption towers containing charcoal or fuller's earth be connected to the breather pipes with the expectation that the absorbent would pick up the gasoline from the exhaled vapors during the day and give it back to the inhaled fresh air at night if the latter were warmed somewhat. However, laboratory experiments showed that the reversible capacity of charcoal in this respect was so small that quite large quantities would have to be used to handle the breath from a single tank or else that the inhaled air would have to be heated quite hot. Similar tests are yet to be run on fuller's earth, but on the whole the method does not seem very promising.

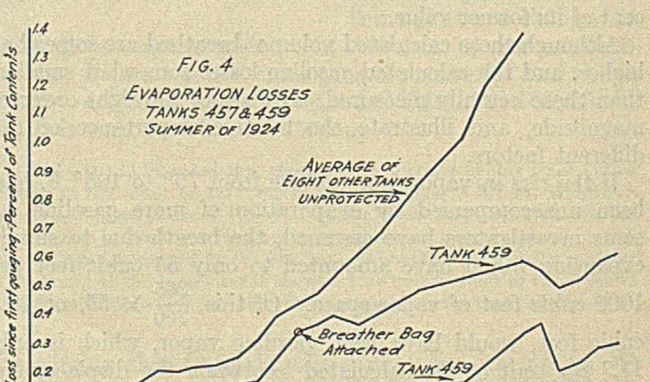
Diffusion Towers. Dr. G. Cash, of this company, suggested that the comparatively great density of the vapors exhaled from a tank might make it possible to collect them during the day by upward displacement of air from a suitable container. On this basis tests were made on three so-called diffusion towers, which consisted of discarded pressure still shells set on end with a series of horizontal baffles inside to prevent excessive mixing of the tank vapors with the supernatant air. These towers did not show any marked savings, either because of the above-mentioned siphoning action which prevented the vapors in the towers from being sucked back at night, or because there was too much mixing.

Gas Holders. A balanced gas holder connected to a system of tanks would have the advantages of large capacity, long life, and low operating cost, and should be practically as effective as a breather bag for conserving gasoline vapors. However, in order not to exceed the mechanical strength of the ordinary steel plate tank roof the holder would have to be counterbalanced to operate at a pressure not greater than 1 inch of water, and if the roof were not absolutely gas-tight an operating pressure which would maintain on the tank roof a pressure balanced within ±0.1 inch of water would be required to prevent excessive losses by leakage. The construction of a holder to operate smoothly at such a low pressure regardless of weather conditions would be very difficult, if at all feasible, and about three times as expensive per tank as a breather bag installation.

Breather Bags. Practically all the objections to these other devices were overcome with the development of the balloon type gas containers or breather bags. These are cylindrical bags made of a closely woven 2 or 3-ounce cotton fabric impregnated with a gasoline-proof mixture of glue and glycerol and connected with the vapor space of one or more tanks so as to inflate with the vapors breathed out from the tanks during the daytime and return the vapor to the tank at night.

Development of Breather Bags

In November, 1922, one of the writers suggested that a flexible gas container for receiving the exhaled vapors from a storage tank could be made of fabric impregnated with some gasoline-proof dope. After much study had been given to the most suitable size, shape, and fabric of the container and the best material and methods for impregnation, during the summer of 1923 two 8000-cubic foot breather bags were built entirely at this refinery. In service these proved very effective and reasonably substantial. For further installations, however, it seemed desirable to have the bags constructed by the aeronautics department of the Goodyear Tire and Rubber Company. After thorough discussion of all features of design, an order was placed for five 18,000-cubic foot containers, each designed to handle the breathing of two tanks. These were installed at different points in the summer of 1924. A summary is given below of the development of the more important features of these breather bags.



Mechanical Features—*Fabric.* After considerable experimentation a closely woven 3-ounce cotton fabric having a

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[7] U. S. Patent 1,489,725 (April 8, 1924).

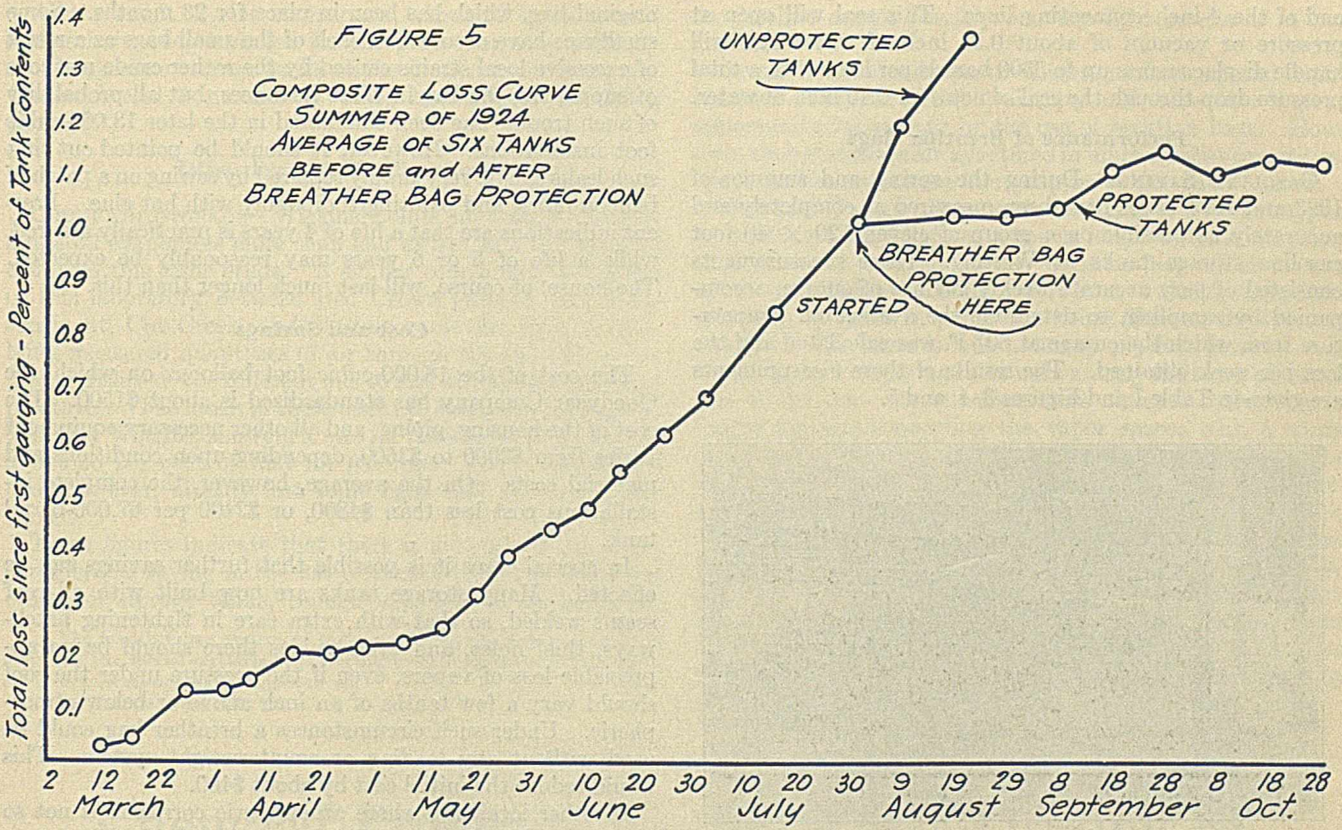

FIGURE 5

COMPOSITE LOSS CURVE
SUMMER OF 1924
AVERAGE OF SIX TANKS
BEFORE and AFTER
BREATHER BAG PROTECTION

tensile strength of about 30 pounds per inch width was selected as most suitable. This is impregnated at an elevated temperature with a special dope consisting essentially of high-grade glue, glycerol, and water. The excess of dope is scraped from one surface, and the cloth chilled to the gelling point of the mixture and dried. The exact composition of the dope was determined after exhaustive tests on the gasoline impermeability and general stability of fully a hundred mixes.

The dried strips are generously coated with talc to prevent sticking and sewed together into the desired shape by machine. A flat seam with $^3/_4$ inch overlap and four rows of stitching has been found satisfactory. The seams are given an additional coat of dope on both sides and this is again dusted with talc.

Design of Breather Bag. Experience has shown that a cylindrical bag with hemispherical ends is the most satisfactory shape. The 18,000-cubic foot bags now being generally installed are 25 feet in diameter with an over-all length of 45 feet. A bag of this size will easily serve two 120 × 40 foot gasoline storage tanks during average summer weather around Chicago.

Housing. Since the fabric of these balloons is by no means waterproof, they must be protected by a weather-proof housing. A wooden frame building with corrugated iron siding and roof has been found satisfactory, but care must be taken to avoid appreciable leaks at the joints and to use high-grade weather-proof ventilators. To hold the balloon in position a 6-inch belly band is attached to its equator, which is clamped securely in a frame fastened to the walls of the house about 11 feet above the floor. When supported in this way the top half of the bag collapses into the bottom half when the bag is empty. This is illustrated by Figure 2. An inlet appendix is provided at one or both ends of the bag, about 18 inches above the floor, and 4-or 6-inch connecting lines sloping slightly downward toward the balloon lead from the tanks or their breather pipes to the inlet appendix. Any condensate in the connecting lines during abnormally cool weather drains into the bag to remain until reëvaporated when weather conditions get back to normal.

LOADING—On account of the shape assumed by the top half of such a balloon during inflation, its operating pressure increases with degree of inflation. Because of the necessity of maintaining balanced pressure under the roofs of tanks that are not absolutely vapor-tight, a loading device with an automatically varying counterweight has been perfected which holds the pressure within a balloon at about 0.25 inch of water throughout the greater part of its operating range. Although this has served its purpose satisfactorily it is not considered necessary on tanks with all welded roofs, and the savings in initial cost and complication to be realized by its omission would justify some extra expense in making roofs absolutely tight which are not at first in this condition.

Table I—Gasoline Losses with and without Breather Bags

	Loss per cent per month
Previous to 1923	
Tanks with spraying but with no breathers:	
Average for storage season	0.43
Summer of 1923	
All tanks having breather pipes:	
Unsprayed tanks, March, April, and May	0.15
Unsprayed tanks, June, July, and August	0.32
Sprayed tanks, June, July, and August	0.22
Tank 459 with breather bag, June 20 to September 20	0.03
Summer of 1924	
No spraying:	
Tank 459, with single breather bag, March 1 to September 30	0.04
Eight unprotected tanks, March 1 to August 30	0.25
Tank 457, with single breather bag, June 4 to September 30	0.07
Tank 459, same period	0.06
Average for unprotected tanks, same period	0.35
Tanks 461 and 462 with balloon	0.03
Tanks 454 and 456 with balloon	0.025
Tanks 453 and 455 with balloon	0.05

SEALS—Emergencies or unusual weather conditions are sure to be encountered when displacement of vapor from a tank or into a tank will exceed the capacity of the breather bag. To provide for such occasions, a tilting liquid seal has been developed to be placed as a safety valve at the tank end of the 4-inch connecting lines. This seal will open at pressure or vacuum of about 0.25 inch of water and will handle displacements up to 5500 barrels per hour with a total pressure drop through the seal of not over 0.40 inch of water.

Performance of Breather Bags

Gasoline Savings—During the spring and summer of 1923 and 1924 losses have been measured as completely and accurately as possible on a group of eleven 120 × 40 foot gasoline storage tanks at Whiting. These measurements consisted of very accurate weekly gagings of outage, accompanied by sampling, to determine the average oil temperature from which the outage at 60° F. was calculated and the loss per week obtained. The results of these measurements are given in Table I and Figures 3, 4, and 5.

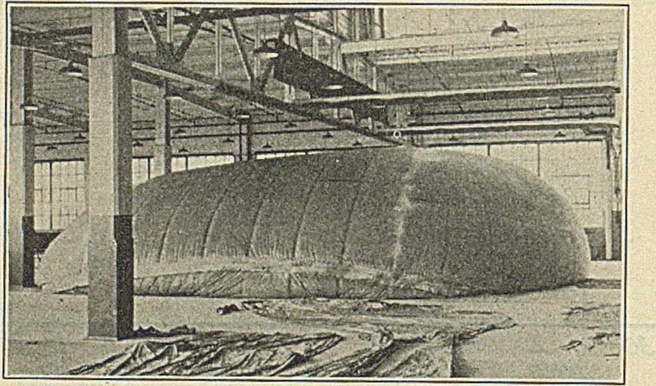

Figure 6—Testing Breather Bag during Construction

The curves show that evaporation losses can be consistently reduced from 0.25 per cent average for unprotected tanks to 0.04 per cent per month throughout the storage season by the use of breather bags.

The early losses from three tanks connected to double balloons were slightly higher than the average of other tanks with similar protection. This was undoubtedly due to leakage through partially opened drain valves on the steam fire lines, which were not discovered until late in the season, and to leakage around the liquid seals before they were perfected. This latter cause was also responsible for a slight increase in loss from one tank with a single breather bag. Hence the composite loss curves for all tanks with breather bag protection, as shown in Figures 4 and 5, are somewhat higher than can reasonably be expected when the above-mentioned defects are corrected.

Capacity—Observations made during August and September, 1924, on a 120 × 40 foot tank connected to a single breather bag indicate that for a maximum vapor temperature rise to 110° F. a breather bag capacity of 7000 cubic feet is ample. To provide for occasional higher maximum temperatures and to leave some margin of safety for periods of steadily rising temperature when the bag will not completely deflate at night, it is planned to allow a capacity of 9000 cubic feet for tanks of this type.

Durability—Samples of the lighter fabric of the first five balloons have been left in the various breather bag houses, where they would be subjected to the same atmospheric conditions and acid fumes as the bags themselves, and occasionally tested for tensile strength, with the following results:

	Lbs. per sq. in.
Cloth before impregnating	18
Cloth freshly impregnated	36
Impregnated cloth after 17 months in balloon house	36

There are now no visible signs of deterioration, such as cracking, peeling, hardening, or molding of the fabric in the original bag, which has been in place for 23 months. Some small rips have occurred in each of the small bags as a result of excessive local strains caused by the rather crude methods of supporting the bag in these instances, but all probability of such trouble has been eliminated in the later 18,000-cubic foot installations. However, it should be pointed out that such leaks can be very simply repaired by sewing on a patch of balloon fabric and painting thoroughly with hot glue. Present indications are that a life of 4 years is practically assured, while a life of 5 or 6 years may reasonably be expected. The house, of course, will last much longer than this.

Cost and Savings

The cost of the 18,000-cubic foot balloons on which the Goodyear Company has standardized is about $1500. The cost of the housing, piping, and all other necessary equipment varies from $3000 to $3500, depending upon conditions and material costs. On the average, however, the complete installations cost less than $4800, or $2400 per 67,000-barrel tank.

In special cases it is possible that further savings can be effected. Many storage tanks are now built with all roof seams welded, so that with extra care in tightening hatchways, thief holes, and cable guides there should be no appreciable loss of vapors, even if the pressure under the roof should vary a few tenths of an inch above or below atmospheric. Under such circumstances a breather bag could be used without any loading or counterweight system. This would reduce the initial cost by about $400.

In other localities, where atmospheric corrosion is not so severe as at Whiting, much lighter metal can be used for covering the balloon house. The use of 27-gage painted black iron saved about $500 over the above figures. Where the roof pitch is lower or the tank roof is insulated it is possible to attach more tanks to a single balloon, thus reducing the cost per tank.

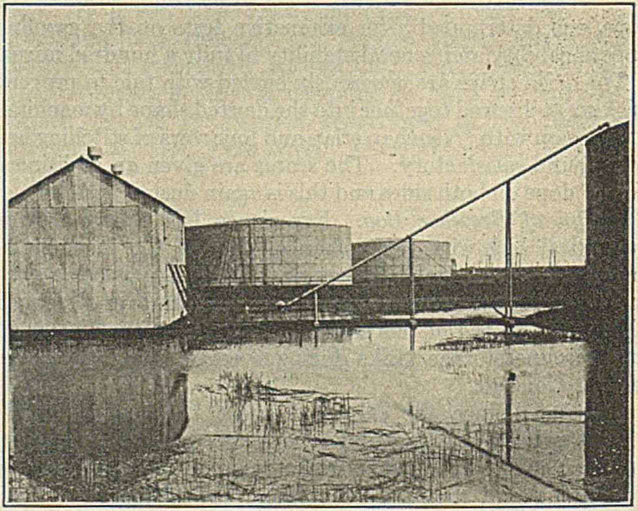

Figure 7—Gasoline Storage Tanks and Breather Bag House for 18,000-Cubic Foot Balloon

The losses from 65,000-barrel storage tanks of gasoline at Whiting averaged about 0.25 per cent per month from March to October, 1924. Breather bags reduced this loss to 0.04 per cent, or a saving of 0.21 per cent or 6900 gallons, which at 10 cents per gallon is equivalent to $690 per tank per month. An 18,000-cubic foot breather bag protecting two 65,000-barrel tanks thus saved $1380 per month under these conditions, paying for itself in 4 months. The savings will, of course, vary somewhat with the climate and the volatility of the gasoline.

As the result of this comparison, about 65 balloons and houses have been installed for the protection of practically all the gasoline storage tanks of the Standard Oil Company (Indiana) and a number of other installations are being planned.[8]

Other Possible Applications

CRUDE OIL STORAGE—Wiggins[9] points out that 35° Kansas crude oil evaporates more than half as fast as a 62° gasoline cut from this same crude. A similar comparison was made in this laboratory between Red Crown gasoline and Mid-continent, Cat Creek, and Sinclair crude oils, both by bubbling measured quantities of air through the oil, and by exposing dishes of the different oils to still air, all at room temperatures. The losses in these tests ran somewhat lower than found by Wiggins, showing a rate for the crude oils averaging about 30 per cent of that for gasoline. The crudes tested had, however, already lost some light ends in storage and transit.

These figures indicate that there is an opportunity for a considerable saving in the use of breather bags on gas-tight crude oil storage tanks, though it is not so promising as on gasoline except possibly on very light crudes or in hot climates.

OTHER LIGHT OIL STORAGE—Light gasolines, special naphthas, etc., because of their volatility and value offer a great opportunity for savings by the use of breather bags. However, such stocks are always stored in much smaller quantities, which makes protection more expensive per gallon saved.

WORKING TANKS—In general, the filling of a receiving pan or working tank displaces a much larger volume of vapor than could be handled by any breather bag which it now seems practicable to build. However, working tanks are generally operated in pairs, one being filled as the other is emptied. The same is true at many pipeline stations. If the filling and emptying rates were exactly the same all vapor loss except that due to temperature changes could be prevented by interconnecting the vapor spaces with a single outlet so that the vapor displacement from one becomes the intake of the other. It is rare that such a perfect balance prevails, the system as a whole generally having a small periodic displacement and intake. This net vapor volume change from a pair of tanks can frequently be taken care of by attaching a breather bag to the above-mentioned single outlet. The possible savings to be effected in this way appear to be very large, and several such installations have already been made, with considerably greater savings per balloon than on gasoline storage.

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[8] The breather bag system of tank protection, the fabric, the liquid seals and the special methods of protecting working tanks are all covered by U. S. patents or pending applications.

[9] *Bur. Mines, Bull.* **200**, 95.

Chemical Problems in the Water Driving of Petroleum from Oil Sands[1,2]

By P. G. Nutting

U. S. GEOLOGICAL SURVEY, WASHINGTON, D. C.

IN THE Bradford petroleum district about 85,000 acres once held about 35,000 barrels per acre of high-grade crude in a layer of fine-grained oil sand averaging perhaps 30 feet thick lying roughly 1200 feet down from the valley bottoms. The oil sand is practically level. About 800 feet above it is a water sand carrying abundant potable water. The oil wells are cased down past the water sand. The rusting through of an old casing, letting water down into an old oil well, is said to be responsible for the modern practice of water driving between rows of wells 150 feet apart.

The older methods of drilling and pumping permitted a recovery of about 15 per cent of the oil. Dissolved gas and the more volatile components of the petroleum itself push the oil along the pores toward regions of lower pressure. It is a nice problem for the chemist, physicist, and mathematician in coöperation to determine the production curves. Solubility, initial pressure, vapor pressure, porosity, viscosity, and time are the important factors involved. Even near the wells, however, not only are the grains still coated with oil, but the pores remain full of oil, since dead oil will not drain from oil sand—the capillary forces are far too great relative to gravity. Complete recovery can be accomplished, if at all, only by displacing the oil by another fluid possessing a greater affinity for sand grains than itself.

Systematic water driving as at present practiced calls for wells 150 feet apart. The drive is about 2 inches per day, or 30 months for the 150 feet. The recovery is 15 to 20 per cent of the original oil. A test boring in the Bolivar, N. Y., tract showed 64 per cent of the oil still in the ground after the water drive had been completed. This method would pay handsomely in spite of the enormous expense of drilling so many wells if the yield were better; as it is, the margin of profit is not very great.

Experimental

Either oil or water will wet silica or glass, and the first experiment was a test of selectivity. Two pieces of glass that fit together are placed on a larger piece of plate glass—water under one, crude oil under the other. On sliding the two pieces together the water quickly displaces the oil if its supply is maintained. On the other hand, if the water supply is limited and the oil in excess, the oil will not drive out the water but will creep around the edges. This experiment shows that water in contact with glass will displace oil in contact with glass irrespective of gravity or of pressure head.

Clean sand in one arm of a U-tube, if saturated with oil, may be freed from oil rapidly and completely by water displacement provided the water be fresh. If, however, the water used has been a week or two in contact with oil it will give a slow ragged drive, and if forced through will leave much oil behind it in the sand. This effect was first noticed in a 0.2-mm. capillary tube filled half with water and half with oil. After a few days the oil and water were found to be side by side each extending the full length (5 cm.) of the tube. Although fresh oil and water are more or less of the cat-and-dog order, after a few days in contact each becomes saturated with the other—about 0.02 per cent of each is soluble in the other—and they become quite friendly. This observation is of vital importance in the water-drive prob-

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[1] Received July 25, 1925.

[2] Published by permission of the Director, U. S. Geological Survey.

lem, since oil and water must remain for a long time in contact with but very little convection.

Another experiment indicates a possible explanation of this odd behavior. Two glass plates are cemented about 0.2 mm. apart and some fine, dry sand is sifted between. If now oil is added at one side and water on the other, a microscope will show sand grains adhering to the oil-water interface on the water side but not on the oil side. In other words, silica wet with water will adhere to oil but the reverse is not true. Coal grains will adhere to the oil side, as will also sand grains wet with heavy hydrocarbons.

If a layer of oil is placed on water in a test tube or bottle and a pinch of clean sand is dropped in, it will penetrate the oil and cling to the under side of the oil coating. As soon as the silica touches the water, it develops an affinity for oil amounting to the weight of roughly a million molecules per molecule surface. The practical problem of water drive is, then, to find a fluid or solution in which silica grains will lose this affinity for oil. For, obviously, if the sand will release its hold on the oil, the oil may be readily driven along away from each sand grain. Given such a medium, it is only a question of keeping up the supply with sufficient head to maintain it. The medium, of course, must not react with the oil and hence become used up, and must not clog the pores of the oil sand.

Theory and Application of Results

Silica in contact with water would naturally be supposed to attract to its surface the hydrogen ions from the water, forming a coating of SiOOH radicals. This hypothesis is familiar to soil chemists. The SiOOH being insoluble, the reaction ceases with the formation of a surface layer. Now SiOOH, like COOH and SOOH, may be supposed to have an affinity for various hydrocarbons, CnHm where $m = 2(n \pm p)$. For example, analogous to $CH_3.COOH$ we might expect $CH_3.SiOOH$ to be formed. But since the latter reaction is limited to a surface layer, we should expect it to be manifest as an affinity in selective absorption. Hence wetting with water may produce in a sand an affinity for petroleum.

This affinity for oil should therefore be destroyed by dissolving in the water a substance having a stronger affinity for SiOOH than that possessed by the hydrocarbons. Many such substances—acids, alkalies, and esters—will weaken the hold of the sand on the oil. But the stronger acids and bases react more or less with the oil; some appear to have a curdling effect. Detergents such as soap form a solid substance which tends to clog the pores. All these substances will be used up and for that reason alone would be unsuitable for water driving in the field, since the oil-water contact face cannot be reached after the start except by diffusion. Weak organic acids such as tannic and acetic might be used, but they are quite expensive.

The affinity of sand grains for hydrocarbons is completely destroyed by the use of a salt of a strong base and a weak acid, in particular the carbonates, bicarbonates, borates, silicates, acetates, etc., of the elements of Group I. Sodium carbonate is particularly effective, is extremely soluble, and is inexpensive. The impure form sold as washing soda is fully as effective as the refined chemical.[3] The reaction with SiOOH is evidently decisive, being perhaps the intermediate step in the formation of sodium silicate. Soil chemists write $SiOOH + OH = H_2SiO_3$ for the surface reaction. This will give a hydrogen replaceable by sodium.

Sand in water saturated with dissolved or emulsified oil at once starts collecting the oil on its surface. Oil standing on water over and in a bed of sand will diffuse downward through at least several millimeters of clear water and gather in droplets on the sand grains in the course of a few days. Sodium carbonate in solution in the water inhibits this action, probably by saturating the affinity of the silica surface; it is hardly plausible that it prevents solution of oil in water.

Many petroleums after standing at rest for a few weeks on water develop a sort of loose interfacial membrane. Even coarse sea sand will be suspended as in a hammock. This membrane appears to be in the nature of the higher alcohols, $C_nH_m.OH$. It is destroyed and inhibited by the addition of sodium carbonate to the water. It appears to have no connection with the attractive forces discussed above.

Oil sand consists of 85 to 98 per cent quartz grains firmly cemented by silica, as a rule, in the Appalachian fields, by carbonates and silicates in the softer sands of the western fields. Occasional grains of calcite and muscovite are not rare. After ignition, 5 to 15 per cent is removable by boiling hydrochloric acid. Grains of the sands of the middle Appalachian field (Franklin to Bradford) are entirely coated with a greenish gray ferrous silicate, which turns red on heating. According to soil chemists, silica grains commonly have an inner coating of hydrated ferrous aluminium silicate insoluble in water and an outer coating of a water solution of water-soluble salts. Apparently, oil sand usually possesses a similar inner coating but an outer coating of oil-soluble hydrocarbons.

The effect of such molecular coatings on the water-drive problem may well be asked. In the absence of knowledge of their precise chemical nature, no chemical theory can be formulated. Much careful chemical work on oil sands remains to be done. However, driving tests with prepared sands show that crude oil may be driven from sand coated with ferric oxide, or even from iron filings, quite as readily as from clean silica. Sand coated with ferric hydroxide or sand containing considerable carbonates also drives well, but not quite so readily. Sands having an over-coat of heavy unsaturated hydrocarbons yield to the sodium carbonate solution slowly, but become clean if given sufficient time.

A test for selective filtering gives a good indication of the best driving speed. An oil sand is crushed and washed with ether, then dried and sifted (65 to 100 mesh) and used in a U-tube drive. If the first oil to come through is very much lighter than that entering, a selective coating of the sand grains with the heavier hydrocarbons is indicated and a correspondingly decreased rate of drive is best. The writer has had a nearly black oil come through but 7 inches of prepared sand as light in color as a canary glass. Chemically purified quartz sand or sand made from crushed rock is almost lacking in this property of selective filtering for most crudes. The property evidently depends largely upon the nature of the under coating discussed above.

Further Work

The sodium carbonate water drive is being given field tests in the Bradford district. Many months will be required to determine its value. Other fields with different oils and different sands and structures may be best worked by modifications of this process or by radically different processes. The investigations are being continued.

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[3] *U. S. Geol. Survey Press Bull.* **2156**; U. S. Patent App. 36,284 (1925).

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The Chemical Division of the Department of Commerce announces two new services based upon surveys of the world trade in naval stores and in prepared medicines. The releases in each series, in mimeograph form, will constitute complete reports covering a single country.

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Artificial Silk[1]

With Special Reference to the Viscose Process

By M. G. Luft

The Industrial Fibre Co., Inc., Cleveland, Ohio

Solutions of baffling problems seldom result in radical changes in the methods of manufacture; nevertheless the chemist is seeking exact knowledge of what occurs in each step of a process. Such is the desire of the manufacturer of artificial silk, one of the youngest branches of the chemical industry. It is approaching its fulfilment but is still in need of assistance from chemical and mechanical research. Research work results in a better product obtained at a lower cost, an achievement always desirable to a chemist.

The manufacture of artificial silk is a good example of an industry in which the technic is considerably in advance of the theory of the process, which at the present time is based largely on empirical research. The literature on the subject is very fragmentary, as most of the research so far has been carried out by the manufacturers and remains unpublished; similarly, the patent literature contains little, if any, information of scientific value.

Artificial silk represents art and refinement in textiles. The advance in art education and artistic taste called for radical changes in development of textiles. By the study of art in schools and encouraged by many publications, art museums, and organizations such as the Art and Industries Foundation, the educated portion of the population created a demand in recent years for more lively and artistic combinations of color, luster, and design of texture. The post-war period stimulated the desire for light and color, resulting in a renaissance of the textile industry. This, combined with the higher buying power of the public and the increased knowledge of manufacture, is the source of the tremendous growth of the artificial silk industry.

This new fiber is not a substitute for natural silk, but is a distinct textile product, as is wool, silk, cotton, or flax. We see how the silkworm produces the silk fiber, feeding on mulberry leaves, and this natural process we are reproducing in a chemical and mechanical way, using also cellulose as the raw material and spinning the solutions of the cellulose compounds. The worm changing from the caterpillar to the chrysalis stage in spinning its cocoon ejects through two extremely fine spinnerets in its mouth a semiliquid viscous substance which on leaving the glands hardens immediately upon contact with the air. It is composed of two albuminous substances containing about 80 per cent fibroin and 20 per cent sericin, the latter being a soluble gum.

History

Rèaumur[2] in 1734 suggested the imitation of natural silk by human artifice. This idea was forgotten until 1855, when the Swiss, Andemars, patented a process of spinning ether-alcohol solution of nitrocellulose by dipping a pointed steel rod into the solution and pulling a thread. In 1882 Swan, Wyne, Swinburne, and Powell produced nitrocellulose threads for carbon filaments for use in incandescent lamps, but their process was not commercially successful. In 1884 Count Hilaire de Chardonnet conceived the idea of forcing a collodion solution through fine capillary openings and he patented a manufacturing process in the same year. The nitrocellulose solution was forced through minute holes into a precipitating bath and the fine filaments were wound in groups. This product was not yet denitrated and therefore very inflammable. The year 1891 witnessed the beginning of the manufacture of artificial silk on a commercial scale in Besançon, France, by the Societé Anonyme pour la Fabrication de la Soie de Chardonnet. In 1890 Despaissis dissolved cellulose in an ammoniacal solution of copper hydroxide, but it was not until 1897 that Pauly was able to start the production of cuprammonium silk. In 1892 Cross, Bevan, and Beadle[3] discovered sodium cellulose xanthate, the compound formed by the action of carbon bisulfide on mercerized cellulose, which they named "viscose" on account of its high viscosity. This discovery was the start of the viscose process of artificial silk manufacture, which today is used more widely than any other. About 80 per cent of the total world production of artificial silk at present is made from viscose and this growing industry is well established in the United States and Europe. About the same time Cross and Bevan produced the acetate esters of cellulose which became the basis of another artificial fiber known as acetate silk.

Kinds of Artificial Silk

These four processes are still used today, having in common cellulose derived from wood or cotton as a raw material. They also have in common similar manufacturing procedures—namely, chemical and textile operations. Tables I and II show the preparation of raw material and the four different kinds of artificial silk manufacture.

Table I—Preparation of Raw Material

Cotton Seed	Spruce Wood
Cleaning	Barking, cleaning, and chipping
Crushing and pressing	Sulfite (Sulfur-lime, calcium bisulfite)
Raw linters	Cooking in digestors
Digesting with caustic soda	Washing and screening
Washing	Bleaching (Lime-chlorine)
Bleaching (Lime-chlorine)	Washing
Washing	Paper machines
Drying	Drying
Bleached linters	Cellulose (Cut in sheets)

Table II—Kinds of Artificial Silk

Nitrocellulose (Chardonnet silk)	Cuprammonium Silk (Also called Glanzstoff or Pauly)
Purified cotton	Purified cotton or wood pulp dissolved in ammoniacal copper solution
Sulfuric and nitric acids	Spinning solution
Nitrocellulose Dissolved in alcohol and ether	Coagulated by caustic soda or sulfuric acid
Filaments coagulated Nitrocellulose filaments	Filaments of cellulose
Recovery of solvents	Bleaching
Removal of nitro groups	Commercial thread
Unbleached thread Bleaching	
Commercial thread	

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[1] Received March 6, 1925. Part of address delivered before the Chemical Club of Princeton University, January 29, 1925.

[2] "Histoire des Insectes (1734–1742)."

[3] British Patent 8700 (1892).

Table II—(*Concluded*)

ACETATE SILK	VISCOSE SILK
Cotton or wood pulp purified	Bleached spruce pulp or
Acetic anhydride, acetic acid, and sulfuric acid	cotton linters caustic soda
Dissolved in acetone	Soda cellulose Carbon bisulfide
Spinning solution	
	Soda-cellulose-xanthate Water
Acetate cellulose filaments	
Commercial thread	Viscose solution Spinning solution
	Crude viscose filaments
	Removal of sulfur Bleaching
	Commercial thread

Nitrocellulose Silk

Nitrocellulose silk is made by treating cellulose in the form of cotton linters with a mixture of nitric and concentrated sulfuric acids. The resulting product, consisting largely of trinitrocellulose, is washed until neutral, hydro-extracted, dried slightly, and dissolved in a mixture of alcohol and ether. This collodion solution after filtration is forced by pressure through very fine glass nozzles. In the dry system the collodion on emerging from the spinneret loses the ether and alcohol by evaporation, leaving the formed filament of nitrocellulose. In the wet system the collodion is passed through a water solution known as a "setting bath." Several filaments are spun together and they form, after the twisting process, the thread consisting of nitrocellulose.

The alcohol and ether eliminated from the solution by evaporation in the dry system, or by dilution in the wet system, are partly recovered and used again as solvents for nitrocellulose. The resulting thread is inflammable and is denitrated by a treatment with sodium hydrosulfide, leaving pure cellulose fibers, which are then washed, bleached, and reeled into skeins. The nitrocellulose process is quite expensive on account of the high cost of the chemicals used. If the denitration is not perfect the silk becomes yellow when stored and does not take the dye evenly.

Cuprammonium Silk

In the cuprammonium process the copper hydroxide unites with the cellulose to form an adsorption compound which is soluble in ammonia. The resulting product has the following composition: 2.5 to 3 per cent copper, 7 to 8 per cent ammonia, and 7 to 8 per cent cellulose.

This process was developed on a commercial scale about 1900 and was used largely in Germany for Pauly or Glanzstoff silk. The solution of cellulose in ammoniacal copper oxide is unstable and must be kept at low temperatures approaching the freezing point of water. It is spun in a manner similar to that of nitrocellulose by the wet system, the solution being forced through fine orifices or spinnerets into a setting bath of dilute sulfuric acid. It can also be spun in a caustic soda solution and the copper removed afterwards from the fiber by treatment with dilute sulfuric acid. The copper silk is then bleached and purified until a product is obtained which is very soft to the touch and possesses high luster. Most of the copper silk plants have gradually changed over to the viscose process. In the United States several attempts have been made and are still being made to manufacture artificial silk by the copper process, but as yet they have not been successful. The last company in England to use this process was the Kent Silk Mills, which has abandoned it recently and has changed to the viscose process, claiming that the cost of manufacture is about 50 per cent less.

Acetate Silk

Acetate silk is the acetic ester of cellulose. Cellulose is treated with acetic anhydride and glacial acetic acid in the presence of concentrated sulfuric acid and a catalyst. It is difficult to produce a homogeneous acetyl cellulose as the acetylation goes too far, resulting in a mixture of di- and triacetates. The acetate cellulose is then precipitated by water, washed until neutral, dried, and dissolved in acetone. After the filtration the solution is spun either in warm air or in a setting bath of water or a salt solution, the former process allowing the recovery of the expensive solvents. The resulting fiber is not a regenerated cellulose, but an acetate of cellulose which does not adsorb moisture so readily as the other kinds of artificial silk. Therefore, it has less affinity for dyes, this property prohibiting, so far, its use on a large scale in the textile industry. Acetate silk is sold under the trade names Celanese and Lustron.

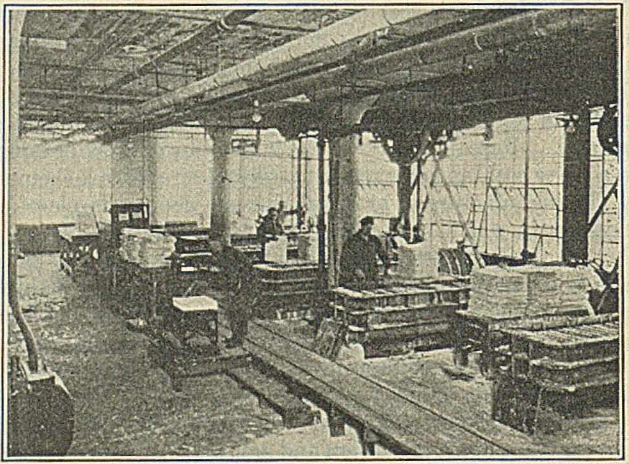


Figure 1—Hydraulic Presses for the Mercerization of Cellulose

Viscose Silk

The raw material used in the viscose process is bleached spruce pulp, bleached cotton linters, or a mixture of the two. The silk made from pulp has a mild, not opalescent luster, and dyes more uniformly than thread made from cotton, because the latter is a more highly polymerized body and therefore more resistant and less active than bleached sulfite pulp. The pulp, cut in rectangular sheets, is soaked in an 18 per cent caustic soda solution. This treatment causes the fibers to swell and an unstable compound of soda and cellulose is formed which is known as soda cellulose. The excess of caustic soda solution is removed by means of hydraulic pressure (Figure 1).

It is very important to maintain the concentration and temperature of the solution and the time of soaking the same from batch to batch to obtain a uniform product. Also, the amount of caustic soda solution remaining in the cellulose should be constant—viz., about two parts of solution to one of pulp. Thereafter the sheets of soda cellulose are placed in shredders, the rotating blades of which operating against a grating grind the soda cellulose into a fine crumbly state. (Figure 2) The heat developed in the shredding of soda cellulose is removed by circulating brine through the jacket of the shredder, thus maintaining the soda cellulose at a constant temperature. The shredded material is conveyed to small containers and undergoes a so-called aging process at a constant temperature for a period of time. The soda cellulose has an increased affinity for dyes and greater reactivity than cellulose, but it is an unstable compound, the character and the velocity of the decomposition being a function of time and temperature. Table III illustrates the change that soda cellulose has undergone during a period of observation of over one year. The two samples were kept at a constant temperature in air-tight containers and at various intervals analyses were made.

Table III—Effect of Aging

(Figures in per cent)

	Sample 1				*Sample 2*			
Time of aging	NaOH	Na_2CO_3	α-Cellulose	Hemicellulose	NaOH	Na_2CO_3	α-Cellulose	Hemicellulose
1 day	14.3	0.7	28.0	0.4	14.1	0.9	28.0	0.8
2 weeks	13.4	1.2	26.1	2.3	13.4	1.3	26.6	1.9
12 weeks	9.5	4.0	23.9	4.2				
64 weeks					1.2	11.4	15.5	14.3
72 weeks	1.5	13.0	15.7	12.5				

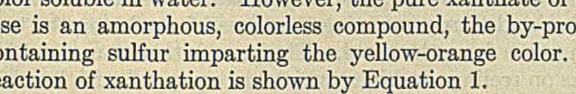
In the aging process the uniformity of temperature, time of aging, and size of the containers are important factors, as they determine certain properties of the resulting viscose and the subsequent steps of the manufacture. The aging of soda cellulose can be accelerated by oxidation and there are several methods known which make use of catalysts for this purpose.[4]

XANTHATION—After the soda cellulose has been properly aged it is transformed into xanthate of cellulose, a reaction similar to ester formation of cellulose. This operation takes place in double-jacketed, air-tight containers (Figure 3), where the soda cellulose is acted upon by carbon bisulfide as the barrels rotate slowly, and the excess heat of this exothermic reaction is removed by cooling brine circulating through the double jacket. Length of time and uniform temperature are also important factors of the xanthate reaction. During this process the white soda cellulose is changing color, which indicates the progress of xanthation. The final product of the reaction is a sticky, amorphous mass of orange color soluble in water. However, the pure xanthate of cellulose is an amorphous, colorless compound, the by-products containing sulfur imparting the yellow-orange color. The reaction of xanthation is shown by Equation 1.

$$C_6H_9O_4.ONa + CS_2 = NaS.CS.OC_6H_9O_4 \tag{1}$$

The resulting cellulose xanthate is readily soluble in caustic soda, giving a viscous orange-colored solution called in the industry "viscose." The product is labile and is decomposed by acids, acid salts, and ammonium salts, or if left by itself for a long time it is regenerated to cellulose hydrate. This reaction continues until equilibrium is reached, which takes place quantitatively under special working conditions. The decomposition is spontaneous, the by-products after the formation of cellulose hydrate being caustic soda, carbon bisulfide, and polysulfides.

The freshly prepared cellulose xanthate is transferred from the tumbling barrel to a mixer containing dilute caustic soda. The mixers are iron tanks equipped with revolving arms, and by means of a cooling device the solution is kept at a low, uniform temperature. After the solution of the xanthate is completed, the liquid is pumped to the ripening department, where it remains at a low, uniform temperature for a period of time until the ripening of the viscose is effected, a process similar to the aging of soda cellulose described before. It undergoes polymerization, during which the xanthate forms larger complexes by splitting off the sodium and sulfur compounds (Reaction 2).



$$S{=}C\left\langle\begin{matrix}O{-}C_6H_9O_4\\ S{-}Na\end{matrix}\right. \longrightarrow S{=}C\left\langle\begin{matrix}O{-}(C_6H_9O_4)_4\,(OH)_3\\ S{-}Na\end{matrix}\right. \tag{2}$$

During the aging process the solution of viscose shows a progressive reduction of polarization in presence of increasing alkali concentration. The excess of carbon bisulfide and caustic soda present in the viscose forms at the same time by-products, as shown in Reactions 3, 4, and 5.

$$3CS_2 + 6NaOH = 2Na_2CS_3 + Na_2CO_3 + 3H_2O \tag{3}$$
$$Na_2CS_3 + 3NaOH = 3NaHS + Na_2CO_3 \tag{4}$$
$$CS_2 + 2NaHS = Na_2CS_3 + H_2S \tag{5}$$

The reactions are continuous. The by-products—sulfides, polysulfides, and thiocarbonates—are further decomposed into hydrogen sulfide and free sulfur by the acid solution in the precipitating bath in the next step of manufacture where viscose is transformed to cellulose filaments. The viscose solution is a gel which can be controlled by dialysis, one of the many interesting problems of colloid chemistry connected with the ripening process of viscose solution. The transition of the cellulose xanthate from the relatively small molecular condition to the semiliquid state whereby the small molecules are polymerized is a change that is visible under the ultramicroscope. During the ripening the viscose is filtered several times to obtain a uniform solution and to remove impurities such as iron, undissolved fibers, etc., which would block the fine holes in the spinnerets. The point where the viscose is sufficiently ripened and ready to be spun is determined for each batch by a simple laboratory method of precipitation. At this stage the cellulose xanthate is polymerized and, being less soluble than when freshly prepared, it can be decomposed and solidified in the spinning process, delivering a uniform product. Finally, the air bubbles accumulated in the viscose are removed by vacuum and the purified solution is transferred as a continuous flow to the spinning machines to be converted into filaments.

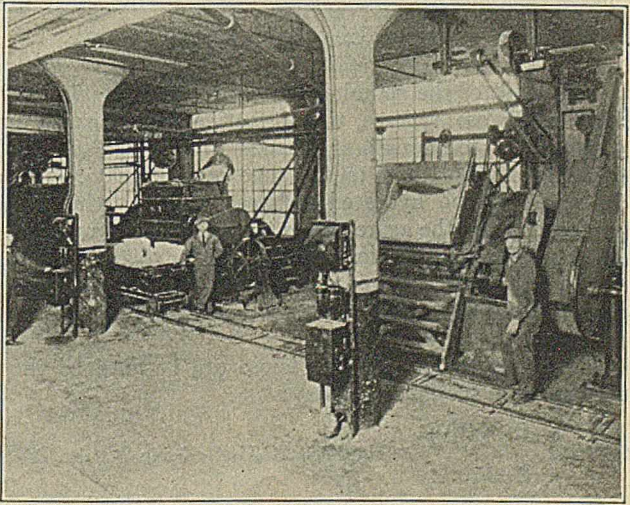


Figure 2—Shredders

SPINNING—Under uniform pressure, undergoing final filtration, the viscose is delivered through mechanical regulators or pumps placed on the spinning machines, each regulator pumping a constant amount of viscose to the outlet fitted with a platinum spinneret. The solution forced through the minute holes of the spinneret is divided into very fine streams which, passing through the precipitating bath, are immediately coagulated and the streams of viscose solution are converted into fine filaments of regenerated cellulose. The reaction that takes place when the alkaline viscose solution is spun or precipitated occurs in two stages: first, the precipitation of the cellulose xanthate caused simultaneously by the salts present in the setting bath and the neutralization of the excess of alkali by the acid also present in the bath; and second, the decomposition of the cellulose xanthate to cellulose hydrate by the prolonged action of acid. The semiliquid state of the coagulated product allows the for-

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[4] British Patents 13,003 (1914); 14,675 (1914).

mation of filaments which in diameter correspond with the minute holes of the jet through which the solution of viscose has been ejected under pressure. During the precipitation an elevated temperature of the spin bath is desirable in order to accelerate the coagulation. There is also a relation between the surface tension of the thread and the concentration of the coagulating medium. The size of the spun thread is determined by the amount of viscose solution of known cellulose content projected through the jet in unit time, and the rate at which the thread is wound on the spool or collected in the centrifuge box, which usually is about 50 meters per minute.

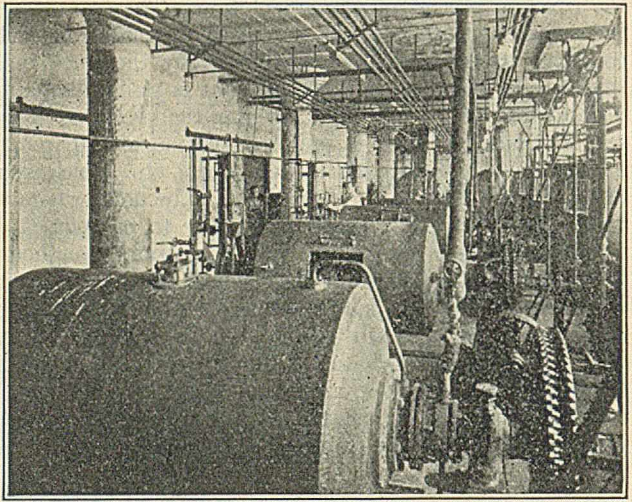
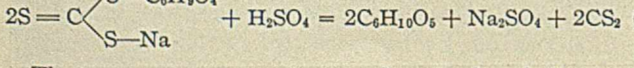


Figure 3—Tumbling Barrels

The result of the spinning process is the formation of insoluble cellulose hydrate, this formation being directly proportional to the strength and temperature of the acid in the precipitating bath and to the time of immersion. During the spinning the hydrated cellulose complex while under tension changes the aggregate of the molecules in presence of acids, resulting finally in an amorphous structure. During the hydration the cellulose filaments are swelling, a phenomenon similar to the previously described process of mercerization.

The spinning reactions of viscose can be outlined in the final stage in the following way:



$$2S=C\left\langle\begin{matrix}O-C_6H_9O_4\\S-Na\end{matrix}\right. + H_2SO_4 = 2C_6H_{10}O_5 + Na_2SO_4 + 2CS_2 \quad (6)$$

There are numerous patents and methods relative to the chemical composition of the setting bath and the spinning apparatus.[5] The two systems of spinning viscose fiber used today in the industry are the spool and centrifugal or box systems, both continuous operations. The precipitated or newly formed fibers are somewhat gelatinous and are slightly stretched by winding on rotating spools or by passing over revolving glass rollers before entering the spin box. In the centrifugal system the spin boxes are rotated at a speed of about 6000 revolutions per minute, and this continuous uniform tension of the rotating centrifuge produces uniform luster of the filaments and simultaneously the individual filaments are twisted together. In the spool system the individual filaments are placed on the spools parallel and therefore must be twisted on separate machines, the resulting twist being more uniform than if produced in the spin box.

The coagulating bath must be kept at a constant temperature and at a uniform strength and composition during the continuous process to prevent filaments adhering to one another and to obtain a uniform product. The orifices of the jet are round, but the cross section of the filament depends on the composition of the setting bath. According to the patent of Stearn,[6] the spinning bath containing ammonium chloride or ammonium sulfate precipitates a filament which appears under the microscope as a glassy cylinder. However, the modern tendency in the fiber silk industry is to produce a rather elliptical or flat filament in the form of a ribbon, which can be obtained by a more rapid precipitation of the cellulose. The spool system uses a spin bath containing dilute sulfuric acid and inorganic salts such as Glauber's salt, whereas the centrifuge system employs sulfuric acid, zinc salt, and glucose.

After the coagulation the viscose thread, which is now an irreversible colloid in a hydrated condition, is washed carefully with water to remove acids, salts, and other components of the setting bath. Furthermore, it is necessary to dehydrate the thread under tension, which prevents contraction in drying and produces a bright lustrous fiber.

After washing, if the spool system has been employed, a twist is given which makes the yarn stronger owing to the friction of the filaments and also prevents the single fibers from being broken, which would produce fuzzy silk. The usual twist applied to the yarn is two and one-half turns per inch and is produced on double-fronted twisting machines where the spools are placed on fast rotating spindles driven by an endless belt. During the rotation the yarn delivered to the take-up spools is twisting between the spin spool and the fixed point represented by the take-up spool or bobbin. The next operation is the setting of the uniform twist by humidification, causing the single filaments to adhere to one another and thus preventing the thread from losing the twist when taken from the spool. The yarn is then converted into skeins on reeling machines, which are equipped with breaking devices to stop the reels, should a thread break. Counting clocks are provided for each reel to measure the yardage, allowing only a definite length to be reeled into a skein. After the proper length of yarn is reached, the clock device stops the reel and the frame with the completed skeins is removed.

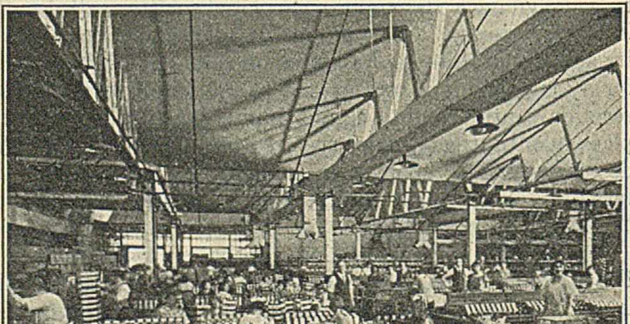


Figure 4—Twisting and Reeling Rayon

The skein is made in such a manner that diamond formations are present at regular intervals. Tie bands made of

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[5] Worden, "Technology of Cellulose Esters," **1921**; Cross and Bevan, "Cellulose," **1918**; Becker, "Die Kunstseide," **1912**; Suevern, "Die Kunstliche Seide," **1920**; Margosches, "Die Viskose," **1906**; U. S. Patent 836,452 (1906); British Patent 163,817 (1920).

[6] U. S. Patent 716,778 (1902); British Patent 1022 (1898).

cotton thread or artificial silk waste are inserted to keep the threads in their proper place, and thus prevent tangling of the yarn when the skein is later wound on cops, spools, bobbins, or quills. These are the usual forms adopted by textile industries employing artificial silk for weaving, knitting, and other textile operations (Figure 4).

During the spinning of viscose sulfur is formed, part of which remains in the silk as an impurity and is removed by the following process. The skeins are treated in the bleaching department with sodium sulfide solution whereby polysulfides are formed and removed by washing with water; then the silk is bleached with chlorine. The latter operation is very delicate, requiring careful control of the chlorine content and temperature of the solution to prevent the destructive oxidation of the cellulose. After bleaching antichlor is applied, the skeins are washed until all chemicals are removed, and the excess of water is extracted in centrifuges and the skeins dried.

INSPECTION AND WRAPPING—From the drier the skeins enter the inspection department, where each skein is examined and graded for quality, great care being taken to see that the silk absorbs a uniform amount of moisture from the atmosphere. Finally, after all manufacturing operations described have been completed, which cover a period of about 15 days, the skeins are wrapped and bundled under pressure in 10-pound packages ready for shipment.

YIELD—From one ton of bleached sulfite pulp 1500 pounds of silk are obtained, the cost of wood pulp being about 5 cents a pound and the present market price for Grade A viscose artificial silk, $2 per pound. This illustrates the earning power of research which, based on the ingenuity of chemists applying intricate methods, is able to increase many times the value of the basic material. To obtain uniformity of product the preparation of the cellulose solution and the spinning of the fiber must be continuous, 24 hours a day and 7 days a week, which makes the performance of an efficient organization extremely difficult.

Properties of Artificial Silk

The finished yarn must possess maximum covering power and sufficient tensile strength. Table IV shows the strength and elongation of different kinds of artificial silk as compared with natural silk.

Table IV—Comparison of Artificial and Natural Silks

KIND OF SILK	Dry tenacity Grams	Wet tenacity Grams	Elongation Per cent
Copper	1.3	0.5	12.5
Nitro	1.48	0.31	15.5
Viscose	1.75	0.75	20.0
Natural	2.5	2.0	21.0

There are several known methods for improving the strength of artificial silk: one, by applying dilute mineral acids and drying in moist atmosphere;[7] another, by increasing the number of single filaments during the spinning process, each filament being proportionately finer whereby the covering power of the yarn is increased. Table IV shows that artificial silk loses strength when in a wet state, because it absorbs readily about three parts of water to one part of cellulose, thereby increasing in volume by 40 per cent; when dried it contracts and regains its previous volume and tensile strength. This absorption and desorption of water is due to the capillary structure of the cellulose silk. If textile products of still greater strength are required, artificial silk is mixed with cotton yarn or natural silk and a large amount of this fiber is used today in mixtures with other yarns.

There are also several known methods for waterproofing of artificial silk, perhaps the most important being that of Sthenose, based on treatment of the yarn with formaldehyde and lactic acid.[8] The silk treated according to this process is more resistant to water owing to the replacement of water by formaldehyde, but at the same time the silk becomes hard and its affinity for certain dyes is decreased. Other methods known for waterproofing of viscose silk are based on treatment with mineral compounds during the desulfurization.[9]

The great power of absorption of moisture is an advantage of viscose silk because when used for underwear, as is done today to a large extent, it absorbs the perspiration from the body and permits the evaporation of the excess moisture due to the large surface of the filaments, thus keeping the skin dry and comfortable. This hygienic property has but recently been recognized and artificial silk combined with cotton or real silk is used more and more as an ideal yarn for shirts and underwear. It has still another advantage in this respect because natural silk rots from perspiration and turns yellow, whereas artificial silk remains white. Natural silk is generally weighted with metallic salts, usually of tin—in some instances, as in black fabrics, up to 300 per cent of the original weight of the yarn—and this content of foreign matters makes the silk brittle and not conducive to good health. Artificial silk, however, is never weighted. It is a pure cellulose product and therefore has no injurious effect on the skin. The gloss and brilliancy of artificial silk surpasses that of natural silk and all other fibers because the individual filaments are flatter and expose a greater light-reflecting surface than natural silk fibers which are cylindrical. Figure 5 illustrates microscopic pictures of a viscose filament compared with other kinds of fibers.

The different kinds of artificial silk have not the same luster, nitro silk being shiny, copper silk glassy, and viscose silvery more like natural. Moreover, the feel of viscose silk is similar to the natural but slightly colder and harsher to the touch. The scroop of natural silk can be reproduced by passing finished viscose yarn through a weak solution of acetic, tartaric, or lactic acid. The softness of the fibers can be further increased by a larger number of single filaments, which are usually coarser than the natural, but for special purposes they can be spun as fine as cocoon filaments. The specific gravity of artificial silk is 1.5, that of natural 1.4.

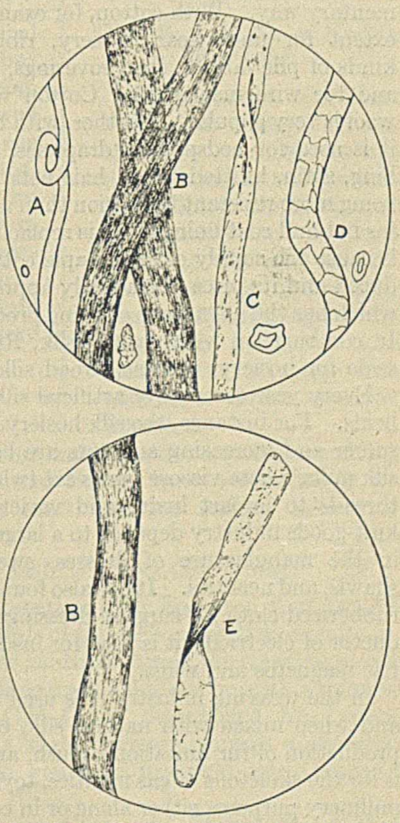

Figure 5—Magnified Approximately 125 Diameters
A—Natural silk
B—Artificial silk
C—Cotton
D—Wool
E—Wood pulp

Artificial silk may be identified by its chemical and physical properties. If mixed in fabrics and highly sized, together with natural silk or cotton, it must be washed, freed from oil,

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[7] Zaenker and Schreiber, Laboratorium der Färbereischule in Barmen.

[8] Worden, "Nitrocellulose Industry," 1911.

[9] U. S. Patent 1,404,535 (1922).

boiled in water, and the individual threads separated before the test is made. The simplest one is the combustion test. Cellulose burns with a flame without odor like cotton or paper, and leaves no residue except a small amount of ash, whereas natural silk, wool, and other animal fibers smoke without burning, giving off a disagreeable odor resembling burnt horn and leaving a charred residue. Gases given off by combustion of animal fibers are alkaline to litmus paper; those of artificial silk are acid. Natural silk and wool dissolve in a 40 per cent solution of caustic soda, cellulose silk swells slightly but does not go into solution. The different kinds of artificial silk may be identified by treatment with pure concentrated sulfuric acid and iodine, whereby nitro cellulose silk dissolves with a purple color, cuprammonium with a light blue, acetate with a yellow color, and viscose silk with a dark blue color.

Application

Artificial silk, which is now called in the trade "Rayon," is used independently of other textile fibers or in a supplementary way. With cotton, for example, it is used to a large extent for underwear, hosiery, ribbons, moire, plush, all kinds of pile fabrics, shoe coverings, cloth gloves, umbrellas, and for wire insulations. Cotton warp with artificial silk woof is very popular. Further, with cotton or independently, it is used for bedspreads, draperies, trimmings, elastic webbing, satin, knitted goods, hair nets, laces, embroidery, and, being more resistant to friction than natural silk, it is valuable for hat and coat linings. It is replacing cotton in many fields because the supply of long staple cotton has been greatly reduced and its price is gradually approached by artificial silk, which has the advantage of being produced in endless lengths. In combination with natural silk, Rayon is used on a large scale for hosiery, ribbons, broad silks, and brocades.

Every year the uses of artificial silk are extended into new fields. For instance, the silk hosiery trade is the largest consumer and increasing amounts are being used by the broad silk mills, where viscose yarns are twisted together with other threads to impart luster and variety to the fabrics. The knit-goods industry depends to a large extent on artificial silk in the manufacture of dresses, sweaters, jumpers, scarfs, shawls, and neckties. It has also found use in connection with rubberized cloth for surgical dressings, and being a poor conductor of electricity it is used for insulating purposes on electric magnetos and wires.

In the weaving industry it is used for crepes, mousselines, and when mixed with natural silk, cotton, or wool, for the production of fur imitations, plush, and velvet. Further use is for the skeletons of gas mantles, toys, artificial hair, and for millinery purposes either alone or in combination with metallic cloth. Artificial silk waste is corded, combed, and spun with wool or used alone for fringes, tassels, button coverings, and felt. Artificial horsehair and artificial straw, known on the market as Visca, are also made from viscose.

One of the recognized advantages of artificial silk, especially of viscose product, is the dyeing quality. Viscose silk takes the substantive and basic colors, the latter with or without mordant, very uniformly, giving brilliant colors to the yarn. If fabrics made of cotton and artificial silk or of two different types of artificial silk are dipped in a bath containing two different dyes, two or three color effects are obtained simultaneously, a process known as cross dyeing which is applied to brocades and other fabrics. In printing mixed or artificial silk fabrics, it is possible to produce very elaborate color designs with striking effects at a much lower cost than would be possible if the fabrics were produced by weaving on Jacquard machines.

According to the records of the Textile Division of the Department of Commerce, the domestic production of artificial silk increased from 1.5 million pounds in 1913 to 35.5 million in 1923 and in 1924 to approximately 42 million, representing a value of over 80 million dollars. The world production of artificial silk, especially viscose, is growing rapidly. In 1910 the production was about 17 million pounds, in 1912 about 20 million,[10] and in 1924 the hundred million mark was passed, of which about 40 per cent was produced in the United States. The world production and consumption of this fiber is far in excess of that of natural silk and according to some authorities it is nearly double. The manufacture of viscose silk is today a well-established industry supported by the supply of common and very abundant raw materials and chemicals readily obtainable all over the industrial world, the success of which is based on skilled labor and technical knowledge. It is very well illustrated by the growing domestic production of this commodity which makes the United States independent of imports. The superior quality of the silk made in this country and the efficiency of the manufacturing methods enable it to compete with countries where labor is cheaper. Figure 6 shows the production and consumption of artificial silk and the importation of raw and artificial silk in the United States.

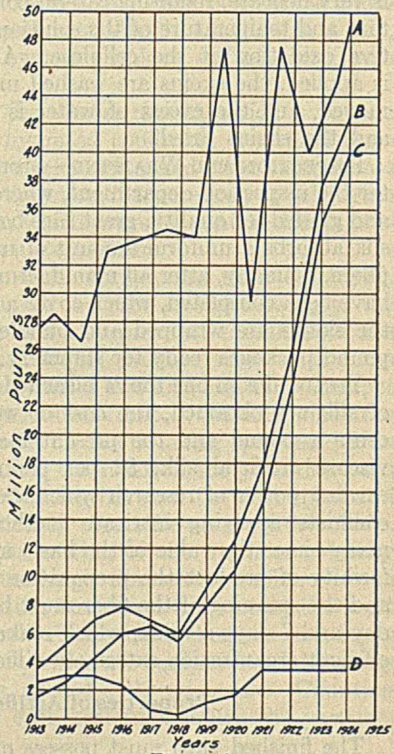

Figure 6

A—Importation raw silk
B—U. S. consumption artificial silk
C—U. S. production artificial silk
D—Importation artificial silk

There are still many unsolved problems open for research in connection with the manufacture of artificial silk—for example, the production of a fiber having greater elasticity and water-resisting properties. This young but growing industry supported by trained chemists and engineers will some day accomplish this task and then unlimited applications will be created for this product of art and science.

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[10] Clément and Rivière, "Matières Plastiques, Soies Artificielles."

New Reflector

A new reflector that is claimed to be as efficient as a freshly silvered glass mirror, that will not tarnish or corrode when exposed continually to the weather, and so hard that the surface can be cleaned with gritty waste without scratching, was described by Robert J. Piersol, research physicist of the Westinghouse Electric & Manufacturing Company, in a paper read before the Illuminating Engineering Society at Detroit, September 15 to 18. The new reflector has a surface of polished chromium and was developed by Dr. Piersol in his search for a reflector that would be satisfactory on automobile headlights and outdoor flood lights.

Glass backed with a silver coating, now the best reflector of light in common use, is not practical for these two purposes, as it is extremely fragile and the cost of its manufacture in the larger sizes is prohibitive.

The reflectivity of chromium is selective to about the same extent as silver, and it is doubtful if the ordinary observer would be able to distinguish between the two.

The Ripening of Viscose[1]

By George de Wyss

The Viscose Co., Marcus Hook, Pa.

The generally accepted conclusion that a chemical change takes place during the ripening of viscose has recently been put in doubt by Leuchs and by Herzog. Investigation of Leuchs's method of analysis showed it to be erroneous. By a modification of it the true amount of xanthate sulfur in viscose can be determined.

This new method of analysis has been tried out on potassium ethylxanthate and on mixtures of potassium ethylxanthate and sodium thiocarbonate. Several viscoses, analyzed when fresh and during the ripening, showed a distinct decrease in the amount of xanthate sulfur, the proportion of sulfur to cellulose falling more than 50 per cent during 160 hours.

Cross and Bevan[2] first advanced the theory that a chemical change takes place during the ripening of viscose. Their method of analysis, in which they separated by-product sulfur from xanthate sulfur by the use of a salt solution, showed a constant decrease of xanthate sulfur, which led them to conclude that the cellulose xanthate, more correctly termed the cellulose ester of dithiocarbonic acid, loses dithiocarbonic acid groups during the ripening, the original $C_6H_{10}O_5$ xanthate resulting first in a xanthate with 12 carbon atoms to one dithiocarbonic acid group, then in one with 18, one with 24 carbon atoms, and finally in regenerated cellulose.

By different ways of analysis Ost, Westhoff, and Gessner[3] and Wolffenstein and Oser[4] came to the same conclusion. On the other hand, Leuchs[5] published experiments which led him to a different view of the subject. He decomposed viscose with sulfuric acid and determined the amounts of carbon disulfide and hydrogen sulfide liberated. Assuming that all the carbon disulfide set free has its origin in the decomposition of cellulose xanthate, and that all the by-product sulfur is liberated as hydrogen sulfide and sulfur, from the fact that he obtained practically constant values for the proportion CS_2: $C_6H_{10}O_5$, he concludes that no chemical change takes place during the ripening of viscose.

In a recent publication Herzog and Hegel[6] came to conclusions similar to those of Leuchs. They likewise studied the ripening of viscose by determining the amount of carbon disulfide and hydrogen sulfide resulting from the decomposition of viscose by an acid, and observed only a slight increase of hydrogen sulfide and a slight decrease of carbon disulfide during the ripening.

Theoretical

As the ripening of viscose is important in its technical use, it was sought to clear away the difference of opinion that exists as to the chemical changes involved. Reflection led to the conviction that Leuchs is wrong in his conclusion that only cellulose xanthate can produce carbon disulfide when viscose is decomposed by a mineral acid, and that therefore the ratio carbon disulfide so evolved to cellulose will indicate how many dithiocarbonic acid groups are combined with the cellulose molecule. Viscose is a solution of cellulose xanthate, in which we find, besides the cellulose compound, sodium hydroxide and the products of the reaction between carbon disulfide and the excess sodium hydroxide—chiefly, sodium thiocarbonate, sodium carbonate, and sodium sulfide. If viscose is decomposed by a mineral acid, the following main reactions take place: cellulose xanthate is hydrolyzed with the formation of regenerated cellulose and dithiocarbonic acid, which latter being unstable decomposes into carbon disulfide and water:

$$ROCS_2Na + H_2SO_4 = ROH + NaHSO_4 + H_2COS_2$$
$$H_2COS_2 = H_2O + CS_2 \qquad (1)$$

Sodium thiocarbonate reacts with the acid to form the sodium salt, carbon disulfide and hydrogen sulfide:

$$Na_2CS_3 + H_2SO_4 = Na_2SO_4 + CS_2 + H_2S \qquad (2)$$

On treatment with mineral acid, thiocarbonates therefore produce carbon disulfide just as well as does the cellulose xanthate, and the proportion xanthate sulfur to $C_6H_{10}O_5$ can by no means be ascertained by simply decomposing the viscose with a mineral acid and determining the amount of carbon disulfide liberated.

Furthermore, if cellulose xanthate decomposes according to the theory of Cross and Bevan, carbon disulfide is regenerated, which would react with the sodium hydroxide to form thiocarbonate:

$$3CS_2 + 6NaOH = Na_2CO_3 + 2Na_2CS_3 + 3H_2O \qquad (3)$$

From this equation, together with Equation 2, it can be seen that at least two-thirds of the carbon disulfide eventually split off from the cellulose xanthate during the ripening would reappear as carbon disulfide upon acidification with a mineral acid. The ratio CS_2: $C_6H_{10}O_5$ as determined by Leuchs would then show only a slight decrease, though a chemical change in the cellulose xanthate molecule were actually involved.

About twenty years ago Cross and Bevan[7] found that cellulose xanthate remains unattacked if treated with a weak acid such as acetic or lactic acid, whereas thiocarbonates are unstable in the presence of these acids. It seemed possible that this property of viscose might be used to modify Leuchs's procedure so as to distinguish between xanthate carbon disulfide and thiocarbonate carbon disulfide. If a dilute solution of viscose is acidified with acetic acid, its color gradually changes from a deep yellow to a very light yellow. This change in color indicates the disappearance of the thiocarbonate. At this moment all the carbon disulfide and practically all the hydrogen sulfide set free by the action of the acetic acid can be removed by extracting the viscose solution with ether. Treated with mineral acid the purified viscose solution still produces carbon disulfide, which can have no other origin than cellulose xanthate. By its determination, therefore, the true amount of xanthate sulfur can be ascertained.

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[1] Presented before the Division of Cellulose Chemistry at the 69th Meeting of the American Chemical Society, Baltimore, Md., April 6 to 10, 1925.

[2] *Ber.*, **34**, 1513 (1901).

[3] *Ann.*, **382**, 340 (1911).

[4] *Kunstseide*, **7**, 28 (1925).

[5] *Chem. Ztg.*, **47**, 801 (1923).

[6] *Kolloid-Z.*, **35**, 196 (1924).

[7] U. S. Patent 717,355 (1902)

Table I

Curve I (Figures 1 and 3)

7.97% Cellulose				6.09% Cellulose				7.49% Cellulose			
Age Hours	% S	S: $C_6H_{10}O_5$	Salt % NaCl	Age Hours	% S	S: $C_6H_{10}O_5$	Salt % NaCl	Age Hours	% S	S: $C_6H_{10}O_5$	Salt % NaCl
0	2.67	1.69	30.0	0	2.31	1.92	30.0	0	2.56	1.73	30.0
39.5	1.68	1.06	16.2	16.5	1.79	1.49	21.1	17	2.08	1.40	21.0
88	1.38	0.88	11.2	22.5	1.66	1.38	17.8	23	1.89	1.28	18.0
117	1.25	0.79	8.6	41	1.51	1.25	14.8	42.5	1.73	1.17	15.4
136	1.13	0.72	6.6	88.5	1.17	0.97	10.2	66.5	1.53	1.03	12.8
				115.5	1.05	0.87	7.6	90	1.43	0.97	10.8
								114	1.25	0.84	8.6
								163	1.07	0.72	4.2

Method of Analysis

One hundred cubic centimeters of a dilute viscose solution containing about 1 per cent cellulose were pipetted into a 250-cc. separatory funnel, acidified with 10 per cent acetic acid, and lightly shaken until the deep yellow color due to the thiocarbonate had disappeared. It was found important to add enough acetic acid to obtain an acid reaction towards litmus. Once the solution had become practically colorless it was thoroughly shaken with 100 cc. of ether. After settling, the aqueous solution was drawn off into a second separatory funnel and again extracted with ether. The aqueous layer was drawn off into a 200-cc. flask, the two lots of ether washed with 25-cc. of water, and the wash water added to the original solution. The flask was then connected through a ground-glass joint with an ascendant condenser and a drop funnel. Attached to the upper end of the condenser was a U-tube filled with pumice stone that had been saturated with a concentrated copper sulfate solution and dried at 120° C. This tube was connected with two U-tubes half filled with a 5 per cent alcoholic potassium hydroxide solution, the last tube being connected with a suction line. Ten to fifteen cubic centimeters of sulfuric acid (1:5) were added through the drop funnel, and a slow current of air was drawn through the apparatus.

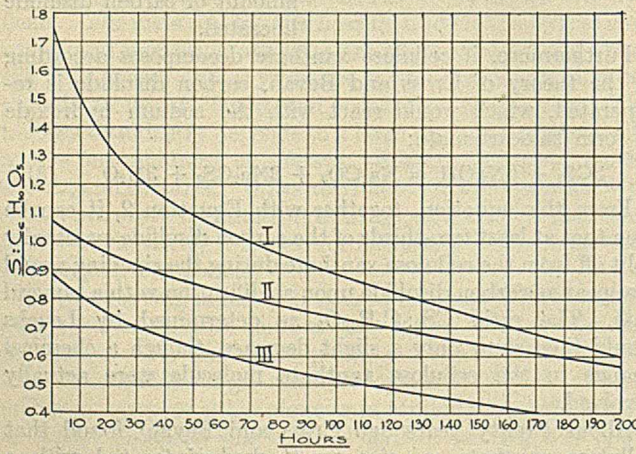

Figure 1—Change in Xanthate Sulfur with Age

At the end of a half hour the content of the flask was heated to the boiling point and kept at this temperature for one hour, in order to expel all the carbon disulfide set free during the decomposition of the cellulose xanthate by the sulfuric acid. The carbon disulfide was drawn through the tube filled with pumice stone, where traces of hydrogen sulfide still present reacted with the copper sulfate, and into the alcoholic potassium hydroxide solution. There it formed potassium ethylxanthate. By means of a water bath the pumice stone tube was kept at 75° C. in order to prevent loss of carbon disulfide through adsorption. The alcoholic potassium ethylxanthate solution was transferred from the two U-tubes into a 600-cc. beaker, neutralized with 10 per cent acetic acid, and after addition of an excess of 5 cc. of acid the xanthate was quantitatively precipitated as copper xanthate by addition of an excess of a 10 per cent copper sulfate solution.

In order to prevent any decomposition of potassium xanthate due to the heat evolved during the neutralization of the alkali, the temperature was kept down by addition of a few pieces of ice to the xanthate solution. After standing for 5 minutes the cold solution was filtered through a Gooch crucible, and the precipitate of copper xanthate washed with water. The precipitate was then decomposed on the filter by 10 cc. of concentrated nitric acid, the filter washed with hot water, and the aqueous cupric nitrate solution evaporated to dryness. The dry residue was taken up with a small amount of hot water, neutralized with sodium carbonate, and slightly acidified with acetic acid. After addition of 1 to 2 grams of potassium iodide, the copper was titrated with 0.1 *N* sodium thiosulfate solution, 1 cc. thiosulfate being equivalent to 0.006357 gram copper or 0.01283 gram sulfur.

Potassium Ethylxanthate

Before this method was applied to viscose it was tried out on potassium ethylxanthate, the sulfur content of which was exactly known. By adding a solution of sodium dithiocarbonate to the ethylxanthate solution the effectiveness of the acetic acid and ether treatment could be determined. As a control the potassium ethylxanthate was first analyzed by straight precipitation as copper salt in acid solution. The results were as follows:

	Substance Gram	Thio. Cc.	Sulfur Per cent
Theory for $C_3H_5OS_2K$			39.95
Straight precipitation	0.5025	15.69	40.08
	0.5816	18.09	39.91
Treatment with acetic acid and ether	0.4986	15.46	39.79
	0.5040	15.89	40.43
10 cc. Na_2CS_3 solution added	0.5053	15.76	40.04
20 cc. Na_2CS_3 solution added	0.5229	16.39	40.25
10 cc. Na_2CS_3 solution added, no acetic acid and ether treatment	0.4986	30.49	78.47

These figures show that the carbon disulfide resulting from the thiocarbonate can be eliminated quantitatively by the treatment with acetic acid and ether, and that the xanthate carbon disulfide set free by the mineral acid can be caught quantitatively in the alcoholic potassium hydroxide solution.

Table II

Curve II (Figures 1 and 3)

7.8% Cellulose				7.6% Cellulose			
Age Hours	% S	S:$C_6H_{10}O_5$	Salt % NaCl	Age Hours	% S	S:$C_6H_{10}O_5$	Salt % NaCl
0	1.68	1.09		2	1.54	1.03	
20	1.56	1.01	10.4	24	1.37	0.91	10.0
43	1.37	0.89	8.6	29	1.32	0.88	9.2
48	1.36	0.88	8.2	50	1.27	0.85	7.6
90.5	1.18	0.77	5.7	95.5	1.13	0.75	4.6
116.5	1.08	0.70	4.2	119	1.06	0.71	3.8
140.5	1.03	0.67	3.4	144	0.98	0.65	2.8
165	0.95	0.62	2.5	149	0.97	0.65	2.7
216	0.81	0.53	0.6	191.5	0.85	0.57	1.3
				197	0.81	0.54	1.0

Viscose

When different viscoses were analyzed during their ripening at 18° C., fairly concordant results were obtained with viscoses made under practically the same conditions. (Tables I, II, and III) The three curves in Figure 1, representing the averages of two or three different viscoses, show a decided decrease in the ratio S: $C_6H_{10}O_5$. Curve I represents viscoses made with an excess of carbon disulfide in order to get as near as possible to the ratio S: $C_6H_{10}O_5$ equal to 2:1. The two other curves were obtained with viscoses made with less than the theoretical amounts of carbon disulfide. Curve I shows that more than 50 per cent of the total decrease occurs within the first third of the time of observation, and a similar tendency is observed in the other curves. It is apparent, then, that the initial rate of decomposition is faster, probably involving the change of the C_6 stage to the C_{12} stage.

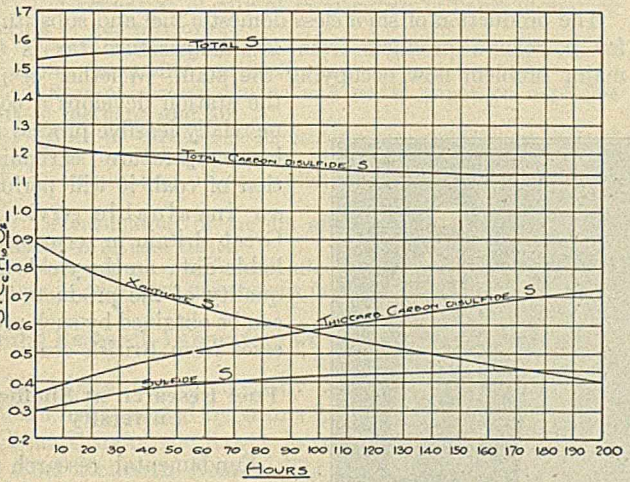

Figure 2—Change in Xanthate and By-Product Sulfur with Age

In Table IV and Figure 2 are shown results where total carbon disulfide S, xanthate S, and sulfide S were all determined for the same viscose during ripening. By decomposing the dilute viscose solution with mineral acid without first treating it with acetic acid and ether, the total amount of carbon disulfide S was determined. This represented the sum of xanthate S plus the amount of thiocarbonate S set free as carbon disulfide according to Equation 3. By deducting the amount of xanthate S from the amount obtained for total carbon disulfide S, the value of this thiocarbonate S was obtained. The amount of sulfide S was also determined by adding 25 cc. of the dilute viscose solution to an excess of 0.1 *N* potassium iodide-iodate solution, which had previously been acidified with sulfuric acid, and titrating the excess iodine with 0.1 *N* sodium thiosulfate solution. This sulfide S represented the sulfur present as sulfide plus the amount of thiocarbonate S set free as hydrogen sulfide (Equation 3). Thereby five curves were obtained. The values for total S obtained by adding those for total carbon disulfide S and sulfide S remain practically constant. The curve for total carbon disulfide S shows a small drop, whereas the one for sulfide S shows a slight rise, which is in accordance with the results published by Leuchs and by Herzog and Hegel, though they were misled in their interpretation. The values for xanthate S, however, again show a decided drop, those for thiocarbonate–carbon disulfide S increasing correspondingly.

Salt Numbers

The state of ripening was also determined by a method similar to the one published first by Hottenroth,[8] namely, the determination of the concentration of a salt solution necessary to start coagulation of a viscose solution. The average salt number curves (Figure 3) for the same viscoses have practically the same shape as the curves for the ratio S: $C_6H_{10}O_5$. The quick drop at the beginning of ripening is perhaps more marked than in the case of sulfur (Figure 1).

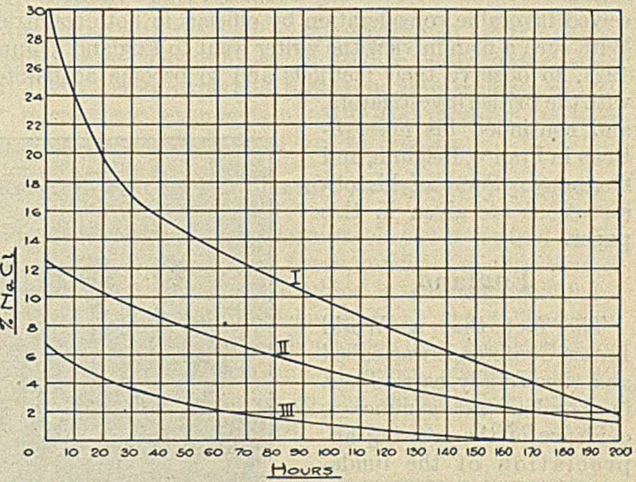

Figure 3—Change in Salt Number with Age

Two samples of viscose were kept at a temperature of 10° C., and it was found that the drop in the values of the ratio S: $C_6H_{10}O_5$, as well as that of the salt numbers, took about four times as long as for viscoses kept at 18° C. This is in accordance with the known fact that increase in temperature hastens the ripening, whereas decrease in temperature retards it.

Table IV

Viscose Containing 8.05 Per cent Cellulose (Figure 2)

	PER CENT S					S: $C_6H_{10}O_5$				
Hours	Sulfide	Xanthate	Thiocarbonate CS_2	Total CS_2	Total	Sulfide	Xanthate	Thiocarbonate CS_2	Total CS_2	Total
0	0.47	1.40	0.57	1.97	2.44	0.30	0.88	0.36	1.24	1.53
67.5	0.64	1.02	0.84	1.86	2.50	0.40	0.64	0.53	1.17	1.57
115	0.68	0.96	0.86	1.82	2.50	0.43	0.54	0.60	1.14	1.57
169	0.70	0.71	1.09	1.80	2.50	0.44	0.45	0.68	1.13	1.57

Conclusions

By the use of Leuchs's method, so modified as to eliminate obvious sources of error, it is demonstrated that the ripening of viscose is attended by chemical changes in the cellulose xanthate molecule, thus substantiating the original conclusions of Cross and Bevan.

The change in the ease of coagulation of the viscose also apparently parallels these chemical changes.

Table III

Curve III (Figures 1 and 3)

7.68% Cellulose				7.3% Cellulose				7.3% Cellulose			
Age Hours	% S	S: $C_6H_{10}O_5$	Salt % NaCl	Age Hours	% S	S: $C_6H_{10}O_5$	Salt % NaCl	Age Hours	% S	S: $C_6H_{10}O_5$	Salt % NaCl
0	1.33	0.88	5.2	0	1.25	0.87	7.0	0	1.31	0.91	7.6
16.5	1.16	0.76	3.8	22	1.08	0.75	5.2	19	1.08	0.75	5.2
64	0.93	0.61	1.8	65.5	0.86	0.60	2.5	115.5	0.70	0.49	0.6
68.5	0.91	0.60	1.6	88.5	0.78	0.54	1.8	162.5	0.61	0.42	0.2
89	0.82	0.54	1.2	112.5	0.70	0.49					
112.5	0.76	0.50	0.6	161	0.59	0.41	0.3				
136	0.71	0.47	0.3								

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[8] *Chem. Ztg.*, **39**, 119 (1915).

Personal Observations on Fuel Research in Europe[1,2]

By A. C. Fieldner

Pittsburgh Experiment Station, U. S. Bureau of Mines, Pittsburgh, Pa.

About two years ago George S. Rice, chief mining engineer of the U. S. Bureau of Mines, proposed some sort of coöperation between this bureau and the British Department of Mines in fuel research, particularly on the prevention of mine explosions and other hazards incident to the coal-mining industry. This proposal received favorable consideration by officials in both countries. With such a plan in view the writer went to England in June, 1924, to observe their methods and to become acquainted with the British investigators, and continued his observations in France, Belgium, and Germany. Some of his observations are given in this paper.

England

The fact that a World Power Conference was called and successfully carried out in London last summer is evidence of the growing appreciation of the fundamental importance of a nation's fuel resources and the need of utilizing this nonreplaceable resource to the greatest possible extent. European governments, as well as industrial associations in the various countries, are showing a greatly increased interest in fuel research since the war. They realize the vital importance of cheap and efficient use of fuel in the growing economic struggle between nations.

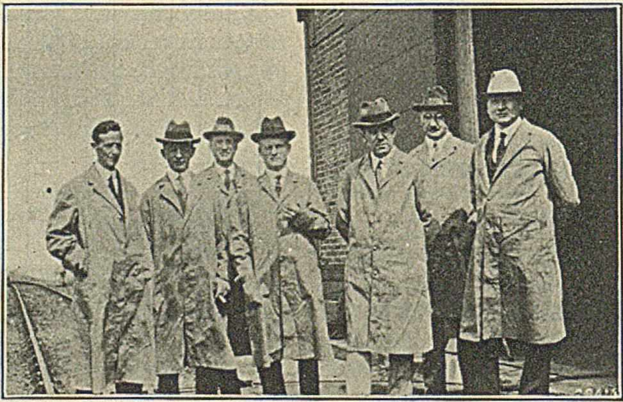

Figure 1—Fuel Technologists from World Power Conference at Fuel Research Station

Left to right—J. G. King, R. Lessing, B. F. Haanel, C. H. Lander, F. S. Sinnatt, Franz Fischer, Professor Purcell

National Fuel Research Station

The British Government appropriated a considerable sum of money before the end of the war to establish a National Fuel Research Station at East Greenwich, London, which is today the largest government-supported experimental station exclusively for fuel research in the world. This station operates under the general direction of the Fuel Research Board of the Department of Scientific and Industrial Research. C. H. Lander is director of the station and Sir Richard Threlfall is chairman of the board. The object of the station is to conduct research along the following fundamental lines:

(1) A survey and classification of the coal beds in the various mining districts by means of chemical and physical tests in the laboratory.

(2) An investigation of the practical problems which must be solved if any large proportion of the raw coal at present burned in its natural state is to be replaced by the various forms of fuel obtainable from coal by carbonization and gasification. The survey of the national coal reserves from the physical and chemical points of view includes: (*a*) exhaustive scientific study of the origin and properties of the chemical compounds of which coal is composed; and (*b*) a practical study of coal beds as they are or might be mined and put on the market. Mine samples are tested, first, by laboratory methods, and, second, by large-scale operations of coking, gas making, etc. The laboratory tests are in some cases made in university laboratories situated in the district, but large-scale tests on the suitability of the coal for carbonization or other methods of treatment are made at the Fuel Research Station.

The production of smokeless domestic fuel and substitutes for petroleum products from low-temperature tar is the major problem now occupying the staff. Whether or not the station develops a commercially feasible process for low-temperature carbonization of coal, it will perform an invaluable service to Great Britain in securing reliable data on the yields and quality of the products that can be obtained by such processes from British coals.

Fuel Research at Sheffield University

Fundamental research on the constitution of coal is conducted in the Department of Fuel Technology of Sheffield University under the direction of R. V. Wheeler. Much of this work is supported by the Safety in Mines Research Board. Wheeler and his associates are attacking the problem of the constitution of coal along broad lines, involving (1) microscopic examination and identification of plant entities; (2) separation of the coal substance into groups by solvent extraction; and (3) treatment of the coal and constituent parts of the coal by methods of destructive distillation, oxidation with reagents, and other chemical reactions. The coal constituents are correlated as far as possible with plant constituents by subjecting these to similar treatment and comparing the results. The microscopic and botanical research is conducted by Marie C. Stopes, at the Imperial College of Science in London.

Recently Clarence A. Seyler, of Swansea, has undertaken the study of the constitution of anthracite. He has developed a wonderful technic in etching polished surfaces of anthracite with chromic acid in such a way as to bring out very clearly the plant structure, when examined under the microscope by reflected light. He has shown identical cell structure in anthracite to that shown by Thiessen of the U. S. Bureau of Mines in thin sections of bituminous coals and lignite when examined by transmitted light.

The tremendous volume of research by Wheeler and his associates on the ignition and propagation of flame in gas and coal dust suspensions impresses one with deep respect for the good judgment of the British Government in supporting true scientific work on the promotion of safety in the coal-mining industry. Furthermore, the fundamental nature of the work makes it of great value to the fuel industry as well. The data obtained on the mechanism of coal-dust explosions are of equal importance in pulverized coal com-

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[1] Presented before the Section of Gas and Fuel at the 69th Meeting of the American Chemical Society, Baltimore, Md., April 6 to 10, 1925.

[2] Published with approval of the Director, U. S. Bureau of Mines.

bustion, as likewise is the work on ignition and propagation of gaseous flames to combustion of gases in industrial furnaces. In the laboratory where this work is done one sees apparatus of very ingenious design for recording flame velocities, measuring pressures and temperatures, and actually taking motion pictures of ignition and propagation of flame through mixtures of gases in tubes and containers of various shapes. The following problems were under way at the time of the writer's visit:

(1) Ignition of gas mixtures by heated surfaces. Determination of time lag and temperature of surface necessary to ignite various mixtures of methane and air, and methane and oxygen.
(2) Determination of relative ease of ignition of various gas and air mixtures by a constant size of flame.
(3) Determination of rate of propagation of flame in moving currents of gas mixtures.
(4) Determination of manner of spread of flame in closed vessels containing flammable gas mixtures.
(5) Effect of carbon dioxide and water vapor on explosive limits of methane and air.
(6) Effect of turbulence in moving air currents on rate of propagation in various mixtures of flammable gases and air.
(7) Determination of static charges on coal dust suspended in air.
(8) Determination of factors affecting the relative ignition temperature of coal dusts.
(9) Determination of factors affecting the rate of propagation of flame in coal-dust suspensions in air.

Mining Research Laboratory at University of Birmingham

This laboratory, directed by J. S. Haldane and J. Ivon Graham, is supported by grants from the Mining Association of Great Britain, the Safety in Mines Research Board, and the Fuel Research Board. The problems undertaken by this laboratory may be classified under three headings: (*a*) general researches on mining problems and utilization of fuel; (*b*) spontaneous combustion of coal; (*c*) control of atmospheric conditions in deep and hot mines.

The general research includes work on the absorption of the gases methane, carbon dioxide, and nitrogen by coal; the physiological effects of carbon monoxide and treatment of carbon monoxide poisoning; and the hydrogenation and liquefaction of coal. The conversion of coal into oil by the Bergius process was the subject of intensive experimentation at the time of the writer's visit. A report on this work has recently been published by Shatwell and Graham.[3]

Researches on the spontaneous combustion of coal have been more extensive at this station during the last fifteen years than anywhere else in the world. Some of the various phases of this problem that are now being attacked are the following:

(1) Measurement of the oxidation and examination of the products of oxidation of various coals and their constituents—fusain, durain, clarain, and vitrain—at temperatures varying from atmospheric up to possible 300° C. under different conditions as regards oxygen supply, special attention being paid to the production of carbon dioxide, carbon monoxide, and water.
(2) Influence of moisture (steam) at higher temperatures in accelerating or retarding such oxidation.
(3) Effect of partial distillation of a coal on its liability to oxidation.
(4) Measurement of the heat production of different coals during oxidation at 100° C. and above.
(5) Investigation of decomposition of oxidation complex and relation of decomposition products to oxygen absorbed.
(6) Influence of adsorption on rate of oxidation of coal.
(7) Other attempts to elucidate the chemical reactions taking part during the spontaneous oxidation of coal by the measurement of the oxidizability of various coals and their constituents after treatment with hydrogen under high pressure.
(8) Practical tests underground with special reference to the application of gas analysis as an aid in the detection and treatment of underground fires.

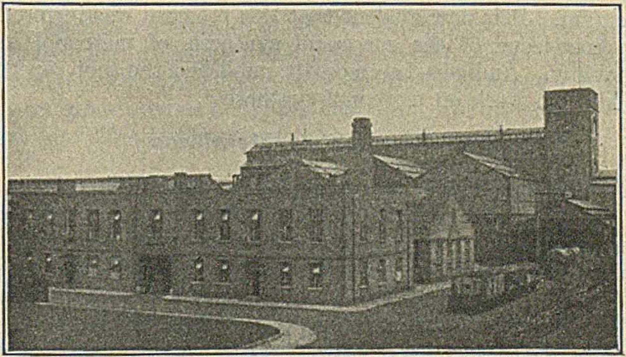
Lancashire and Cheshire Coal Research Association

This association is composed of coal owners in these two mining districts. A laboratory for the investigation of fuel and coal-mining problems is supported at the College of Technology at Manchester under the direction of F. S. Sinnatt, now assistant director of the Fuel Research Station in London. This laboratory has published several bulletins concerned with the methods of sampling and analyzing the coals of the district and in making the necessary tests involved in preventing accumulation of mine gases and in rendering the dust nonflammable by proper application of rock dust. It is also conducting a chemical and physical survey of the coals of this region in coöperation with the Fuel Research Board.

Associated with the work of this association are the Lomax Paleobotanical Laboratories at Bolton, near Manchester. Mr. Lomax is an expert in preparing thin sections of coal for microscopic examination. He has prepared sections across entire coal beds from top to bottom.

Research on Gas Manufacture at University of Leeds

The Institution of Gas Engineers of Great Britain maintains at the University of Leeds, under the direction of Professor Cobb, certain fellowships in gas engineering research. Fundamental problems such as the influence of steaming and method of carbonization and gasification on the liberation of nitrogen and of sulfur, efficiency of gas appliances, heat of reaction in the carbonization of coal, etc., are the subjects of these fellowships. A new experimental carbonization plant consisting of separate batteries, one containing horizontal and the other vertical retorts, has recently been completed.



H. M. Fuel Research Station, East Greenwich, England

Commercial Low-Temperature Carbonization Experiments

Great Britain has undoubtedly led the work in commercial low-temperature carbonization experimentation. The desire to produce a smokeless semicoke for open-grate fires and a home source of liquid fuel has been the urge behind this work. Almost every conceivable method of carbonizing coal has been tried and one finds the same vigorous opinions on the economic possibilities of low-temperature carbonization that prevail in America.

The two processes that are seemingly the nearest to technically successful operation in England are the Parker retort process at Barnsley, and the Maclaurin process at Glasgow. The Barnsley plant consists of two batteries of thirty-two cast-iron vertical retorts each, of a total capacity of 100 tons per 24 hours. The coke is fairly dense, contains 10 per cent volatile matter, and is excellent smokeless fuel for open grates. Complete results of an official test by the Fuel

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[3] *Fuels in Science and Practice*, 4, 127 (1925).

Research Station have recently been published. Whether the process will prove an economic success can only be shown after several years' operation furnishes data on the maintenance costs of the iron retorts, and after commercial returns on the products are definitely established. The Maclaurin retort is an internally heated gas producer type of carbonizer. The gas is necessarily of low heating value and the coke is friable and porous; therefore, less desirable for domestic fuel than the Coalite from the Parker process. However, the retort is much cheaper and should have less maintenance cost.

France

From a national point of view France is intensely interested in securing a home source of liquid fuel. The only possible internal source is coal. The government, recognizing this need, has detailed E. Audibert, director of the French Coal Dust and Explosives Testing Station at Montlucon, also to direct the research of the newly organized National Association of Research for the Treatment of Fuels. This organization includes commercial fuel interests and the government. A new laboratory was being equipped last autumn for experimental work on (1) the Bergius process of hydrogenation and liquefaction of coal, and (2) the production of liquid fuels from some combination of gases—as, for example, carbon monoxide and hydrogen. Audibert proposes to make a comprehensive experimental study of the reactions of these gases at various temperatures, pressures, concentrations, and in the presence of all the different possible catalytic materials that he can think of. Considerations of cost and economic feasibility are not to enter into his research program. It is now evident that this program was inspired by knowledge of the successful synthesis of methanol in Germany. Audibert has recently published the first report of his own work on methanol synthesis.[4]

Fuel Research at Montlucon

At Montlucon is the research laboratory and testing station of the Central Committee of Collieries of France. Aside from mine safety research, M. Audibert is conducting at this station two major lines of fuel research: (1) combustion of pulverized fuel, and (2) the coking properties of French coals when carbonized separately and in mixtures. A part of the work on the combustion of pulverized fuel has been published.[5] The research on coking properties of French coal is prompted by the lack of good coking coals in France. Audibert is endeavoring to determine systematically the swelling and agglutinating properties of the various French coals and mixtures of these coals, as well as the temperature at which softening and swelling of the coal takes place. From these experiments, conducted in small laboratory furnaces, he hopes to obtain data on the most promising blends of French coals for large-scale coke-oven experiments.

Low-temperature coking, according to Audibert, does not interest France, because stoves and furnaces, rather than open grates, are used for house heating. There is therefore no need for a smokeless semicoke. Furthermore, low-temperature tars do not yield much volatile motor fuel, which will eventually be needed to replace gasoline.

Claude Ammonia Process and Ethyl Alcohol from Coke-Oven Gas

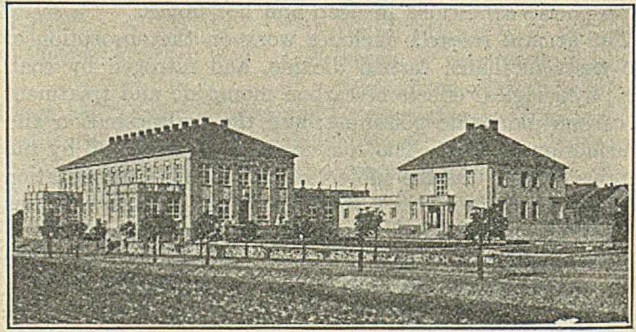
An experimental Claude ammonia process plant of 3 tons per 24-hour capacity was in operation at a coke-oven plant near Béthune in the coal field of Northern France. Work was in progress on making ethyl alcohol from the ethylene, and it was pointed out that the carbon monoxide might be utilized for making methanol by combining it with hydrogen.

Low-Temperature Coking in the Sarre

The only French low-temperature coking experiments were being conducted by M. Saint Claire Deville, technical director of the Sarre Mines at Sarrebrück. The object was to make artificially a low-volatile coke—that is, semicoke—for mixing with the high-volatile Sarre gas coals for the production of a coke suitable for metallurgical purposes. Coke made from straight Sarre coal is friable; only 30 per cent remains on a 50-mm. screen after a drop (shatter) test; but coke made from a mixture containing approximately 12 per cent of semicoke gives 75 per cent on a 50-mm. screen after the drop test.

Germany

In Germany one is at once impressed by the close coöperation of the government, the universities, and the industries. Although the present government does not directly support fuel research, it does actively promote and coördinate the work of a number of research institutes and association laboratories supported by the industries through a Fuel Research and Utilization Committee of the Reichskohlenrat. The two Kaiser Wilhelm Institutes for Coal Research—the one at Mülheim-Ruhr and the other at Breslau—and the Institute for Brown Coal Research at Freiberg are supported by industrial groups in the particular district in which they are located. The directing staffs are in close touch with both the universities and the industries. A large portion of the working staffs of these institutes consists of students from the universities taking their post-graduate research work for Ph.D. degree.



Institute for Coal Research, Mülheim-Ruhr, Germany

Before the war these institutes, as well as the university laboratories, were engaged almost exclusively on fundamental scientific research. But since that time, owing to the loss of their supporting endowments, they have been obliged to turn their principal efforts to meeting the immediate problems of the industry in the substitution of brown coal and inferior grades of bituminous coal for the high-grade Ruhr coals which had to be exported on reparations account.

Kaiser Wilhelm Institute for Coal Research at Mülheim-Ruhr

The leading coal research institute in Germany is the one directed by Franz Fischer at Mülheim-Ruhr, in the heart of the Westphalian coal fields. The problems come under three main headings; (1) the constitution and origin of coal, (2) the coking constituents of coal, and (3) the production of oil from coal. The outbreak of the war within a few months after the completion of the institute naturally diverted the main energy of the first five years of its existence

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[4] *Chimie et industrie*, **13**, 186 (1925).

[5] Audibert, *Rev. ind. minérale*, January 1, 1924.

to the problem of making petroleum substitutes from coal. The small laboratory rotary retort was the forerunner of the large Thyssen and Fellner-Zeigler low-temperature retorts, which were put into commercial operation during the period of petroleum shortage. Research on the composition and utilization of low-temperature tar from various bituminous and brown coals is one of the important current problems.

The most interesting problems, however, were those involving reactions at high pressures. Fischer has developed technic and special apparatus of great variety for extracting coal with solvents at temperatures considerably above the boiling point of the solvent, for oxidizing coal and coal constituents in the presence of various reagents under pressure, for studying the action of carbon monoxide and of hydrogen at high pressures, and for the production of combustible liquids from the interaction of carbon monoxide and hydrogen, in the presence of catalysts at high pressures and temperatures. By these methods of attack he has obtained data supporting the lignin theory of the origin of coal, and has produced Synthol, a gasoline fuel substitute, from carbon monoxide and hydrogen.[6] A problem of practical interest was the isolation of the coking and swelling constituents of coal by extraction of the coal with benzene at 250° C. and treatment of the extract with petroleum ether.[7] Some experimental work on the Bergius process for hydrogenating coal was also in progress.[8]

Upper Silesian Institute for Coal Research

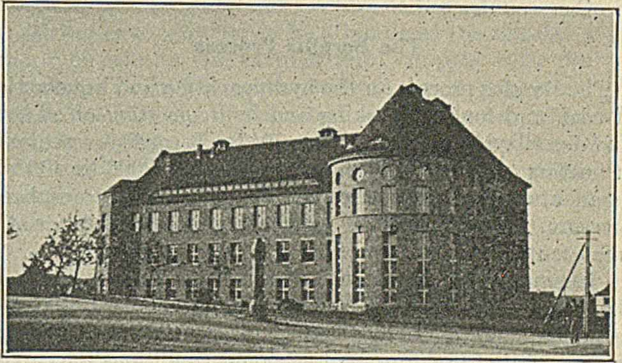
This institute at Breslau was also established for fundamental scientific work on coal, under the directorship of Fritz Hofmann. The staff is engaged on industrial problems of immediate need to the local coal and coke operators. Among the technical problems that have recently occupied their attention are (1) the low-temperature distillation of coal; (2) the blending of Upper Silesian coals for production of metallurgical coke, with special reference to the addition of low-temperature coke to swelling gas coals; (3) the combustibility of coke; and (4) the purification of crude benzene. Dunkel[9] has worked out a method for removing the gum-forming constituents of benzene.

Institute for Brown Coal Research

This institute is located on the southeastern edge of the Central German or Saxon brown coal fields, which have been heavily drawn upon since the war to supply the deficiency in fuels due to occupation of the Ruhr coal fields by the Allies and the loss of a large portion of the Upper Silesian coal fields to Poland. No doubt these losses stimulated the establishment of this institute to engage on the problems incident to the mining and utilization of this low-rank fuel consisting of 50 per cent water.

The work of the institute is in three divisions: (1) mining, under Professor Kegel; (2) fuel technology, under F. Seidenschnur; and (3) chemistry, under R. von Walther. The principal problem in the fuel technology and chemical sections is the carbonization of brown coal. A large-scale experimental plant was in operation at the Reichen Colliery about one mile from the institute building, where experiments were being conducted on carbonizing brown coal and brown coal briquets with hot products of combustion in a unit of 7 tons per 24-hour capacity. The char produced ignites easily and burns with a short smokeless flame, and is said to be superior for domestic use to the "Grudekoks" made by the present style of "Rolle" retorts in general use in the brown coal field. The advantage of this process is said to be larger capacity per unit and a yield of tar equal to that obtained in small laboratory retorts, as compared with only 50 to 60 per cent in the "Rolle" retort.

The chemistry division of the institute is giving particular attention to the examination of the tar, oils, and paraffins obtained from the distillation of the brown coal. The total amount of these tars obtained varies from 6 to 12 per cent of the weight of the raw brown coal. Some coals are much richer in by-products than others. Not all are suitable for distillation. The richer coals yield considerable proportions of paraffin wax. However, the recovery of light oils suitable for gasoline substitutes is not considered practicable in this method of distillation by the sensible heat of circulating gases, owing to the great dilution of the distillation gases by the inert gases used as a heating medium. The tars are worked up into Diesel engine and fuel oils and paraffin wax.



Institute for Brown Coal Research, Freiberg, Saxony, Germany

Teaching and Research Institute of the German Association of Gas Engineers

The German Gas Association maintains a research institute at Karlsruhe, directed by Karl Bunte. The institute is supported by the German gas industry, the amount of money contributed being based on the tonnage of coke produced by each supporting company. Besides conducting more or less fundamental research work of interest to the industry as a whole, the institute does consulting engineering work for the individual companies, for which it is paid by these companies on the basis of actual cost plus a small charge for overhead expenses. Owing to the change in coal supplies as a result of the war, this consulting work has occupied a large part of the energies of the staff. Yet, in spite of these unfavorable conditions for research, Dr. Bunte has been able to carry on a fair amount of fundamental work for publication with the aid of students at the Hochschule taking their thesis work in his department and at the institute.

Some of the research problems in hand at the gas institute were the following:

(1) Investigation of activated charcoal for recovery of benzene and removal of hydrogen sulfide from gas.

(2) Study of exact methods for gas analysis.

(3) Investigation of cause of increase in density of wash oil used in light oil recovery and nature of soluble matter accumulating in these oils in use.

(4) Determination of the reactivity of coke by measuring the air absorbed by the coke after pumping it out in the high vacuum of the mercury diffusion pump, and plotting the absorption capacity of the coke against its porosity, ignitibility, etc.

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[6] Fischer and Tropsch, *Brennstoff-Chimie*, **5**, 201, 217 (1924); see also Fischer, This Journal, **17**, 574 (1925).

[7] *Ibid.*, **17**, 707 (1925).

[8] Fischer, *Brennstoff-Chem.*, **6**, 69 (1925).

[9] *Ibid.*, **5**, 145, 265 (1924).

(5) Determination of the ignition temperature of cokes, by heating the powdered coke in a silica tube through which air is drawn at a constant rate.

(6) Reactivity of coke with carbon dioxide is also determined in a similar silica tube furnace.

(7) Investigation of liquid purification of gas with sodium carbonate, including a study of the equilibria between NaHS, H_2S, HCO_2, and CO_2.

(8) Study of action of pyridine on coal heated to various temperatures.

It will be observed that most of these problems have to do with coke. Dr. Bunte stated that the big problem before the gas industry was to make a more desirable domestic fuel. Evidently, gas coke lacks popularity in Germany as well as in other countries.

The Bergius Process

The Bergius process for the hydrogenation and liquefaction of coal, and for the cracking and hydrogenation of oil, was first described by the inventor in 1912. It consists essentially of heating the coal or oil in an autoclave to 300° to 400° C. in an atmosphere of hydrogen of 100 to 150 atmospheres pressure. About 1919 a commercial size plant for the treatment of oil was built by the Deutsche-Bergin A. G. at Rheinau near Mannheim, Germany. The capacity of the plant is 50 tons of oil daily. It was evident that tremendous sums of money had been spent on experimental work, and that under present economic conditions the capital and maintenance costs are probably too high to compete with existing cracking methods of lower cost and less efficiency.

The large plant has never been used for the hydrogenation of coal. However, a small unit of 0.5 to 1 ton per 24 hours capacity was in operation on coal.

From his own observations and from the work of Shatwell and Graham at the University of Birmingham, the writer believes that the hydrogenation process works, although it is still in an experimental stage. Whether it can be carried on at a profit has not yet been demonstrated. Bergius claims that 1 ton of crude oil can be produced from 2 tons of coal for 30 shillings (then about $6.90), covering interest on investment, amortization, repairs and labor, for a plant in England.

Comparison of American and European Fuel Research

The Fuel Research Station in England reminds one of the Fuel Testing Plant established by the United States Government in St. Louis at the Louisiana Purchase Exposition in 1903. There is a similarity of magnitude and of purpose in so far as surveys of national fuel resources are concerned. However, the St. Louis investigations and the subsequent work of the Bureau of Mines were concerned mostly with the combustion of coal, whereas the British plant is concentrating on the carbonization of coal. American power-plant operators have been quick to take advantage of the results of American government research organizations. The tremendous progress made in modern American power plants has placed them far ahead of most European plants. To an outside observer it appears that the gas and coke-oven industry of England does not keep so closely in touch with the Fuel Research Station as is done in America.

In fundamental scientific research on the constitution of coal and on flame propagation British investigators lead the world, but there is a well-defined gap between them and the industries—a gap that is not observed in Germany, or in America. The close relations between German government and university investigators and the industry before the war is well known. This relationship is even stronger today, since institutional endowments have disappeared and these institutions are obliged to subsist on direct contributions from industry. However, regardless of how fuel research may be supported in European countries, they all recognize the basic nature of the fuel problem in relation to the industrial life of the nation and, bearing in mind the general lack of funds, they are carrying on much more research than our own far wealthier country. The successful development of a synthetic methanol industry in Germany is a sufficient proof of the value of such research.

A Simple Electric Water Still[1]

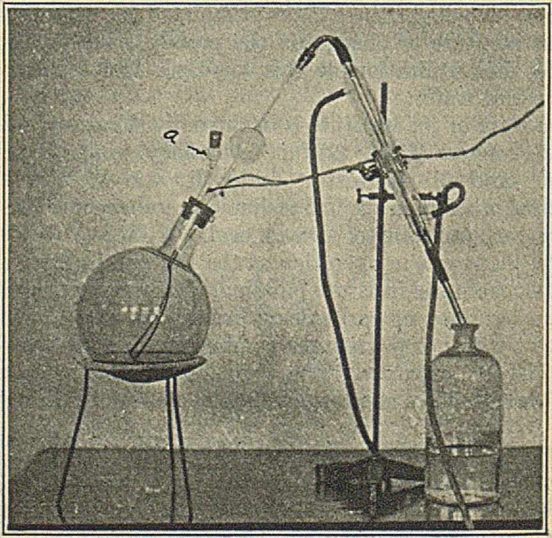
By Ralph W. Gelbach

Washington State College, Pullman, Wash.

THIS apparatus can be operated on the ordinary 110-volt alternating current. Besides being very efficient it entirely eliminates the usual "bumping" which is nearly always present in stills heated by gas or other external methods. This, obviously, tends toward a better quality of water. The best sample obtained with this apparatus had a specific conductivity of 2×10^{-7} mhos.

The apparatus consists of a Pyrex balloon flask connected to a block tin condenser by means of a fractionating column. A 12-liter flask is very convenient, but larger or smaller sizes may be used. The condenser may be constructed by bending a piece of $^3/_8$-inch block tin pipe so as to connect with the still head and passing it through an ordinary condenser jacket. Tube *a* is provided for refilling the still without the inconvenience of disconnecting the apparatus. The heating element is a 20-ohm coil of No. 24 nichrome wire, which is immersed directly into the alkaline permanganate solution and may rest on the bottom of the flask without danger of cracking the glass. The ends of the coil are attached to heavy copper leads, which are passed through the rubber stopper. They are bent in semicircular form in order to space them farther apart and thereby reduce the conduction through the solution.

With a solution containing about 750 mg. potassium hydroxide and 200 mg. potassium permanganate per liter the water is distilled at the rate of 2 liters per hour. The current required for such a set-up is about 11 amperes.



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[1] Received August 3, 1925.

Colloid Chemistry of Color Varnish[1]

II—Pitting, Seeding, Silting, and Surface Dulling

By F. E. Bartell and M. Van Loo[2]

University of Michigan, Ann Arbor, Mich.

A number of the common defects observed in color varnishes are believed to be due to vortex ring action caused by evaporation of volatile. Various defects, such as pitting, seeding, silting, and surface dulling, are discussed from this point of view.

Pitting is discussed from three standpoints—as arising (*a*) from high interfacial tension between the varnish and the surface to which it is applied, (*b*) from the repulsion of the varnish body from nuclei precipitated from the oil body, with the same electrical charge, and (*c*) from vortex action, which may leave the centers of the cells as open pores in the films.

Seeding is believed to be due to (*a*) the accumulation of the pigment on immiscible solids suspended in the oil, (*b*) insufficient wetting of the pigment by the oil body, and (*c*) vortex action, due to the piling up of the denser or larger particles at the centers or corners of the cells.

Silting is considered to be a result of the regular alignment of cells in the varnish film, coupled with the vortex action described under seeding.

Surface dulling is described as due to (*a*) the interference of light from the uneven celled surface of the film, (*b*) the accumulation of the pigment or other immiscible phase at the air interface, and (*c*) the addition of water to the mixed varnishes.

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THE first paper in this series[3] described the celled surface presented by color varnishes on drying, and showed that this structure is caused by the vortex action occurring during the volatilization of the thinner used in varnish. The various stages of the secondary flow occurring subsequent to vortex action, tending to eradicate cell structure in a varnish film, were also described. In the present paper certain defects of varnishes, and more particularly the relation of the vortex motion during the drying of varnish films to these defects, will be discussed.

Pitting

Pitting, the formation of pores or open points in the film, may arise from any one of several different causes. The first is the withdrawal of the film from certain points on the surface to which it has been applied, pointing to a high interfacial tension at these spots. Morrell and de Waele[4] have offered such an explanation, as have others.

If the surface to which the varnish is applied is either damp or greasy, we may expect a high interfacial tension between the two surfaces in contact. This type of defect is not due to the varnish itself, but rather to the mode and place of application, and consequently does not particularly concern us here.

The writers have found varnishes that consistently "pit," regardless of how or where they are applied. Figure 1 shows a carbon black oil varnish that was rejected for its pitting. In making this plate it was necessary to use a very thin film, which accounts for the sparseness of the pigment. All plates of blacks in these papers are perforce of thin films, as otherwise they would be meaningless. Figure 1 shows numerous open areas throughout the film from which both the oil body and pigment have receded, leaving undesirable pits. The varnish was applied to a clean glass slide, free from grease, dirt, or moisture, therefore the foregoing explanation of high interfacial tension does not hold in this case.

Morrell[4] offers another explanation which at times may apply. With certain new varnishes microscopic dispersed particles may deposit on evaporation of the volatile solvent, and each particle or group may act as a nucleus of the same electrical charge as the bulk of the medium. Repulsion around such nuclei would result, giving rise to pitting. The explanation is reasonable, though the writers' plates have shown nothing which they could presume to call nuclei in the pits.

Another type of pitting, for which a logical explanation and remedy can be offered, is that presented in films from which the volatile has evaporated from the centers of the vortices at such a rate that the body of the varnish becomes too viscous to flow into and to fill these voids. As a result the film is left with many of these openings, which detract from the appearance of the film, and render it readily permeable to moisture and weathering effects. Each pit, of course, represents a vortex center—namely, the center of a cell.

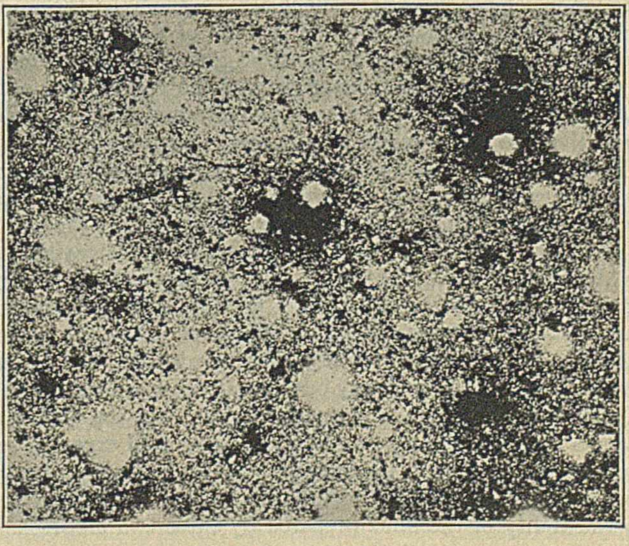

Figure 1 × 150

In another paper[5] the writers have discussed the preparation of membranes with uniform distribution of pores which are formed by vortex action in collodion. Such membranes are commonly used in osmotic work. Since there are so many points of similarity between such membranes and a badly

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[1] Received May 4, 1925.

[2] Holder of the Acme White Lead and Color Works Fellowship.

[3] This Journal, 17, 925 (1925).

[4] "Rubber, Resins, Paints, and Varnishes," 1920, pp. 197 and 198. D. Van Nostrand Company.

[5] *J. Phys. Chem.*, 28, 161 (1924).

celled film of varnish, it is very possible that similar osmotic effects may be obtained in some faulty varnish films. If any moisture were to collect on the surface of the varnish, the presence of electrolytes, either on the surface to which the varnish is applied or in the varnish itself from the driers, etc., would set up the necessary conditions for osmosis. As a result the varnish would lose its qualities as a protective coating and the water would pass through it and loosen the varnish from the surface covered, so that rotting or rusting could proceed. The dried film might then act as a gel and swell by imbibition of water. When the film dried once more, it would be free from the surface to which it had been applied, and the expansions and contractions would usually result in a network of fine cracks which would grow as time progressed. As the light impinging on the varnished surface would then suffer reflection from the numerous surface planes, dulling by interference would invariably result.

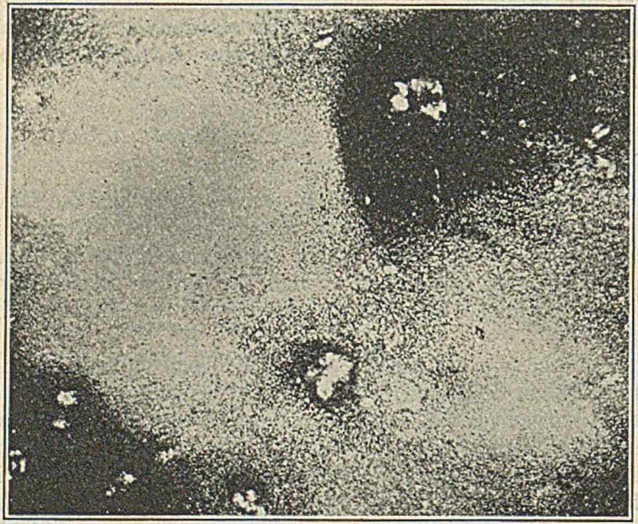

Figure 2 × 150

Since pitting of the type last described is a result of vortex action which produces permanent pores in the films, the eradication of this defect lies in the control of this same vortex action. In overcoming a defect of this nature, one must consider the relative concentrations of the volatile and nonvolatile constituents, the rate of evaporation of the volatile, and the rate of hardening of the film. All these factors influence the degree of definiteness and permanency of the cell structures arising from the vortex action. A varnish that will not show this defect must have such properties that after the volatile has passed off and vortex action has ceased the oil body still retains sufficient fluidity to permit the secondary flow to eliminate the cell centers or pores. A smooth and impermeable film can thus be obtained. Morrell[6] states that films of shellac in ordinary spirit varnish are very porous when dried in the usual way but are quite impermeable when the shellac is applied in the molten state. In the first case active vortex action would occur, and we would expect pores to be formed, whereas in the latter case no such action would be expected. Hence we can readily foresee a difference in permeability of the films prepared by these two methods.

Seeding

Seeding, the objectionable accumulation of the pigment at certain points in the film, may arise from two or three distinct causes. A common cause is the adherence of the pigment to some foreign or immiscible solid in the oil body, such as undissolved or precipitated gums or resins, or some other solid impurity. In a certain carbon black varnish examined by the writers, seeding was excessive; the pigment was piled up badly in certain spots at the expense of the surrounding area, which was quite free from pigment. It appeared that seeding in this film was due to the accumulation of the pigment around certain insoluble solids suspended in the oil body. To test their theory, the writers added to a sample of a good carbon black varnish, a small amount of aluminium palmitate, which was quite insoluble in the oil body and at the same time was a type of compound that one might expect to find in a varnish. Figure 2 shows the result very clearly; each bit of palmitate is heavily surrounded by pigment, while around these spots may be seen areas almost denuded of pigment. The seeding thus obtained was almost like that exhibited by the defective varnish, and the theory seemed substantiated.

In the aging of certain varnishes exhibiting this defect, a heavy skin or film formed at the surface. If this skin was disintegrated and dispersed through the oil body, each fragment served as a nucleus for seeding, but if the skin was removed entirely, the tendency towards seeding was reduced. The solids causing the defect were present in this film or skin. The resin-free acids may be the constituents causing this aggregation of the pigment, because these acids can react with basic pigments to produce soaps of varying degrees of insolubility,[7] leading to seeding as cited above. The mechanics of the accumulation of the pigment on the foreign matter can be explained from either of two standpoints—namely, that of relative interfacial tension, or of relative wetting or adsorption; in the ultimate analysis both explanations amount to the same thing.

The distribution of solids in a liquid medium is often considered a function of relative surface or interfacial tensions. Our varnish system contains, among other things, an oil body, a suspended pigment, and, in the case of this defective varnish, a certain immiscible organic solid. Hence, within the varnish the following interfaces will come into play in seeding effects: immiscible solid-oil, pigment-oil, and immiscible solid-pigment. At first the two solid phases, the pigment and the immiscible solid, are both covered with oil. However, if the interfacial tension immiscible solid-oil is greater than the sum of the interfacial tensions pigment-oil plus immiscible solid-pigment, then the interface immiscible solid-oil must disappear. Since, within the varnish itself it can only be replaced by the interface immiscible solid-pigment, a certain amount of the pigment must adhere to the immiscible solid, displacing the oil. In other words, in case an interfacial tension of a system can be lowered by the accumulation of a constituent of the system at the interface, that constituent will tend to go to the interface. This will account for the accumulation of the pigment around a solid shown in Figure 2.

The same relationships can be considered from the second standpoint, perhaps the better one—that of relative wettabilities. By wettability of a solid we mean the tendency of the solid phase to adsorb the liquid phase surrounding it; in other words, it is a measure of the force of adhesion between the respective solid and liquid phases. Hence, in the light of the foregoing discussion, if the amount of adsorption is low, which means that the force of adhesion is low, the interfacial tension must be high; and conversely, if the amount of adsorption is high, the force of adhesion must be high, and the interfacial tension low. Thus it is evident that the discussions from the two standpoints of interfacial tensions and relative wettabilities are essentially the same.

The immiscible solid has a tendency to adsorb the oil

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[6] Discussion on "Colloidal Chemistry of Paints and Varnishes," *Chem. Trade J.*, **66**, 237 (1920).

[7] Storey, *Drugs, Oils, Paints*, **37**, 392 (1922).

body—that is, to be wetted by it—and the pigment has a similar tendency. Regardless of the relative values of these two forces, so long as there is sufficient oil to wet both solids, there can be no change in the system, provided that only these two tendencies are involved. But further consideration shows that we must include a third, the adhesive force between the immiscible solid and the pigment, and on its relative value as compared with the wettabilities of the solids much depends. If the pigment is wetted more by the oil than is the immiscible solid, and if the adhesional force between the two solid phases is sufficient to permit of the rupture of the interface immiscible solid-oil, then that interface will disappear. This means that the immiscible solid is no longer coated by the oil body but by pigment instead. Therefore, instead of the original series of interfaces, immiscible solid-oil-pigment-oil, we will eventually have the series immiscible solid-pigment-oil, with the excess pigment wetted by oil as before.

Seeding due to the causes discussed above can best be remedied through the removal of the foreign matter or solids, at the base of the trouble. This explains why the seeded varnish first mentioned was improved by removing the surface skin that formed during storage. In other cases settling or straining may serve the same purpose. Otherwise, the only alternative is to change the interfacial tensions in such a way as to reduce the adhesional force between the foreign solid and the pigment.

In other cases of seeding studied, no foreign matter to account for the defect could be detected. Figure 3 shows such a seeded carbon black varnish; the microscope failed to show any immiscible solid present, although the aggregation of pigment was marked. As a further distinction from the first type of seeding, it was noticed that there were no open areas around the seeds. In fact, the distribution of pigment through the oil body was fairly uniform, so that it was concluded that the aggregates of pigment were already existent at the time of application of the varnish.

The explanation of this defect must be that originally the pigment was not properly wetted by the oil. To obtain a thorough and stable suspension of a pigment in an oil there must be the proper preferential wetting—namely, the wettability of the pigment towards the oil must be great. This, of course, means that the interfacial tension between pigment and oil must be low. It is well known that grinding pigments in oils is particularly effective in forming stable suspensions, because the pressure of the rollers aids the normal but insufficient forces of capillarity to insure thorough wetting. In the case of such a varnish as we were last considering, if no means could be found to wet the pigment by the oil body, which it is desired to use, any more thoroughly than in the state illustrated, then a paste of stable consistency should be prepared by grinding the pigment first in an oil with which it shows the lowest interfacial tension.[8] This paste should then be mixed with the regular oil body and a stable suspension would be secured without seeding in the varnish film.

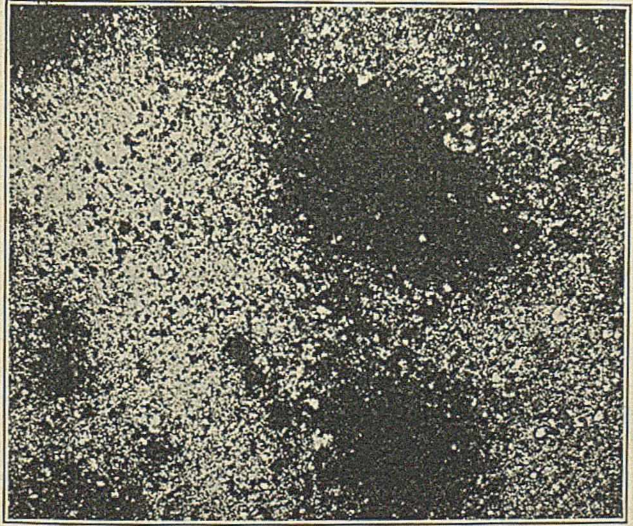

Figure 3 × 150

With certain pigments, especially with carbon blacks, the color bodies are often coated with a greasy layer having such a high interfacial tension towards the oil medium that no wetting is effected.[9] To insure wetting, the volatile must have some solvent action upon this greasy surface, so that the oil body may reach and be adsorbed on the pigment proper. If the interfacial tension between the pigment and oil is low, then this solvent action need proceed only until the oil once reaches the pigment surface, when the interface pigment-oil will entirely displace the greasy layer.

Another type of seeding may be explained through the vortex action. This type is produced by the piling up of the larger particles of the pigment at the centers, or in the corners, of the cells, owing to a resultant of two forces—normal vortex action and gravity. The mechanics of this accumulating effect with large or dense suspended particles is discussed fully by Bénard.[10]

From our knowledge of colloid phenomena we know that particles of sufficiently small size will remain in suspension in a liquid medium indefinitely, apparently in disregard of the ordinary forces of gravity. The phenomenon is dependent on the size and density of the suspended particle, and the viscosity and density of the suspension medium. The velocity of fall of a particle through a medium is expressed in the familiar equation of Stokes:

$$V = \frac{2r^2(S - S^1)g}{9n}$$

where V is the constant rate of fall, r the radius of the particle, S and S^1 the specific gravities of the particle and the liquid, respectively, n the viscosity coefficient of the medium, and g the gravitational constant. By reducing the size of the particle, or by equalizing the two specific gravities, or increasing the viscosity of the medium, the rate of fall is, of course, reduced. Observations bear out the conclusions of the equation. As the size of the particle is decreased the rate of fall diminishes until in very fine suspensions there appears to be no fall whatever, and the Brownian movement is observed. Ebell[11] states that ultramarine blue, which he obtained in a very finely divided state by careful grinding and elutriation, remained suspended in pure water for months.

Hence, if the density of the smaller particles of the pigment does not exceed appreciably that of the medium, they will fulfil approximately the conditions for a stable suspension, particularly since the viscosity coefficient, which appears in the denominator, is comparatively large in case of oil varnishes. Therefore, regardless of its original position in the system, such a particle would persist in the original circuit of the vortex action (as described in Part I),[3] in which it first finds itself. This represents the ideal situation.

However, if the density of the particles is appreciably higher than that of the surrounding medium, and their size not sufficiently small to permit the stabilizing force discussed above to predominate, then the force of gravity will play an important role in determining the path of motion of the individual particle. If we consider all other forces on the particle as balanced during the course of its circuit in the vortex, at certain

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[8] Britton, *J. Oil Colour Chem. Assoc.*, **3**, 131 (1920).

[9] Nuttall, *J. Soc. Chem. Ind.*, **39**, 67 (1920).

[10] *Ann. chim. phys.*, **23**, 62 (1901).

[11] *Ber.*, **16**, 2429 (1883).

points in its path the force of gravity will pull it out from one circuit into the next in continually increasing magnitudes. The friction on the particle is greatest at the wall near the bottom of the cells, and so eventually the centrifugal currents will deposit the heavier particles in a heap at the center, or at the corners, of the cell. Vortex seeding may be readily identified by the fact that the heaps of pigment are quite uniform as to space distribution and size.

The remedy for this defect may depend on one or both of two factors. Equalization of the relative densities of the two phases usually reduces the seeding, or, as before stated, a reduction of the size of the suspended particles may minimize the gravitational effects and eliminate the trouble. Again the importance of careful and uniform grinding in producing a stable suspension required for a good varnish is apparent. Even where ample secondary flow follows seeding by vortex action, it is difficult to flow out the heaps of pigment to uniform dispersion of color, and at best a streaky film usually results. Hence viscosity and oxidation velocity do not concern us so much in this case as they have in others. The pigment itself is the disturbing factor, and on it depends the success of the elimination of seeding of the last type.

Silting

Silting, the accumulation of the pigment along certain lines in the varnish body, resulting in a grained appearance of the film, seems to be associated with a certain regular alignment of cells. Instead of the honeycomb arrangement of hexagonal cells usually exhibited, the cells sometimes tend to become rectangular through the repression of two sides of the hexagon. These cells then line up with their longest sides in contact, forming a uniform series of considerable length in some cases. Figure 4 shows this effect in an exaggerated form; it is a photomicrograph of a varnish film to which a high volatile had been added. The cells tend to be rectangular, although they still show traces of the double Y $\left(\begin{smallmatrix}\mathrm{Y}\\ \curlywedge\end{smallmatrix}\right)$ centers discussed in the previous paper.

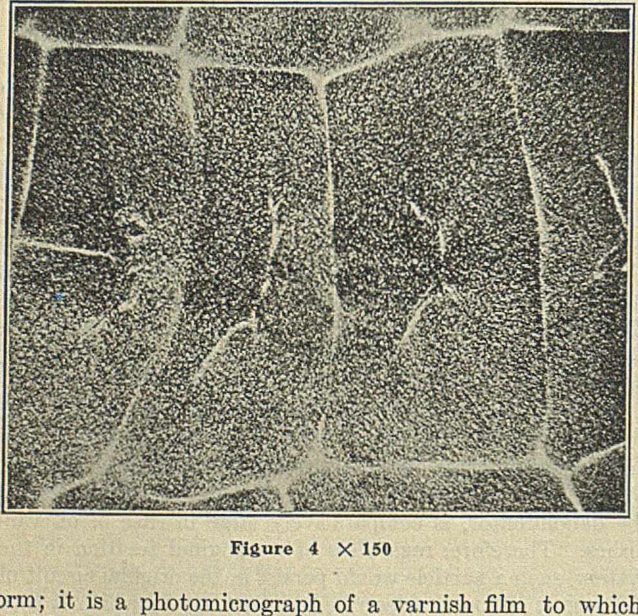

Figure 4 × 150

Silting, of at least one type, appears to be the result of two effects in the film—namely, the regular alignment of cells, and the accumulation of the pigment particles at the vortex centers, as discussed above. When the cells line up as illustrated in Figure 4 the cell walls sometimes are all permanent, but usually, when associated with energetic vortex action, the transverse cell walls in contact across the series tend to disappear. If this occurs, the vortex action is no longer distinctly orientated about individual centers, but all along a line marking the common centers of all the adjoining cells in the series. If there is any tendency for the pigment to pile up at the centers of the cells, because of its density or the large size of the dispersed particles, it is evident that under the present circumstances the pigment will pile up along the line running through the whole series, and silting will result.

When vortex action has ceased, following the evaporation of the major part of the volatile, momentarily at least the line of centers will leave a depression in the film. In order for the oil body to flow into this depression in its secondary flow, it must flow partially from the outside cell walls. This will accentuate the variations in density of color and increase the grained appearance.

In case the coalescence of the cell centers has not occurred to any marked degree, individual pits will remain immediately following the cessation of vortex action. During secondary flow, the varnish will usually flow down through the individual series as streamlines. These pits may catch and retain more than their proportionate amount of pigment, and thus increase the silting effect.

Another point, which has not yet been investigated, concerns a possible relation between the cracking of varnishes and cell structure, dependent upon the effect of pigment on the elasticity of a varnish film. If this factor enters, because of the unequal distribution of pigment, such films will be inclined to crack and to disintegrate rapidly.

If the cell walls are permanent, since they are practically free from pigment their coefficient of elasticity will undoubtedly differ from that of the more highly pigmented areas. These inequalities may lead to cracking due to volume changes during aging, and due to expansions and contractions during temperature variations. This would be true especially of such films as exhibited the regular alignment of cells just described, since in such a varnish the pigmented and unpigmented areas are in regular sequence. The forces in such a film are not so well-balanced as in the average film, and cracks of considerable length could occur. A varnish film first shows a very minute and intricate network of fine cracks, which grow as time progresses until they are large and visible to the unaided eye. It is apparent that we are dealing here, not only with the elasticity of the film, but with cell structure as well, and both must be reckoned with in overcoming excessive cracking.

Surface Dulling

Surface dulling was the defect which originally engaged the attention of the writers in this work. It would appear from their observations that such dulling might arise from more than one cause. The first would be due to the more or less complete interference of light rays impinging on the celled surface of a defective varnish. Figure 5 shows an irregular cell formation in an ultramarine blue varnish film. From the diagrams given in the first paper of this series it is apparent that a varnish surface which is permanently celled is very uneven and made up of the small surface planes of the cells, which are at angles to each other. There is usually no difficulty in observing this ripply surface on a dull varnish, even without a microscope.

The principle involved is simple. Maximum reflection would be obtained from a plane surface (refractive indices being constant) where light interference would be at a minimum. A high gloss on a varnish at least indicates that the surface is smooth. Such a surface is desirable not only because it sheds moisture readily, but also because it is easily cleaned. Again we find the problem of improving dull films of this type centering about the gaging of secondary flow leading to the eradication of the cell configurations. The oil body must flow over and fill in the cell walls and centers after the vortex action has ceased. Satisfactory surfaces of high reflection and gloss would thus be obtained.

The second type of dulling, which appears to be a very common one, is due to the accumulation of a portion of the pigment or other disperse phase at the air interface, uncovered by the oil. Thus the surface presented is similar to that of a powder—a haze covers the major portion of the exposed areas, with a consequent loss of gloss. Close examination shows that the whitish discolorations are often confined to the surfaces of the cells, the interstices between the cells usually being wide and dark. The appearance resembles that of grain leather.

Interfacial tension effects must be responsible for the appearance of such quantities of disperse phase at the surface of the film. On the basis of the discussion of interfacial tension given in earlier portions of this paper, the interfacial tension oil-air (oil representing the oil, volatile, resins, driers, etc.), must be greater than the sum of the interfacial tensions oil-pigment, and pigment-air. Therefore, the interface oil-air tends to disappear through the interposition of the disperse phase. The vortex action occurring through the evaporation of the volatile furnishes an excellent means for bringing the pigment to this position and, once brought there, it remains, owing to the decrease in interfacial tension as discussed above. Thus we account for the appearance of the pigment at the air interface, with the resulting dulling. This defect can be removed by altering the character of the oil body to such an extent that its interfacial tension with air is lowered below that of the interfaces pigment-oil and pigment-air. The surface to which the varnish is applied may also have to be considered in the study of interfacial tensions existing between the phases of the system. In this case the problem is considerably more complicated.

Another type of surface dulling is due to the deleterious effects produced by the addition of even a small amount of water to certain oil varnishes. In their work on ultramarine blue varnishes the writers have found that the addition of less than 0.5 per cent of water to a mixed color varnish may produce a radical change in practically all the properties of the varnish. In every case studied a very viscous emulsion of the water-in-oil type is obtained upon stirring, which is of such rigidity that it would be impossible to brush out the film properly—every brush mark remains as a permanent disfiguration. The viscosity of the system is too high to permit any manifestations of vortex action. When the water, which is now dispersed through the oil in fine drops, evaporates, the whole film is pinholed and the surface in particular is ragged and uneven. The gloss is sharply reduced by the interference of the light rays from this surface. In addition, the pigment tends to accumulate at the interface between the oil and water, so that when the water evaporates from the drops at the surface of the film the surface remaining is really largely made up of pigment, from which the reflection, of course, is poor. Surface dulling of this type is consequently an extreme type, and such varnishes will be found to have lost their desirability as protective or decorative coatings. When water is added to a completely mixed color varnish, all the conditions required for emulsification are satisfied; we have two immiscible liquid phases, oil and water, and the pigment as the solid to build up a stable interface. Consequently, the introduction even of traces of water to such a color varnish must be avoided.

The pigment of these water-in-oil emulsions is generally flocculated. For flocculation of an originally well-dispersed suspension to occur, the particles must be brought together in some way, and in this case the relative interfacial tensions function as the agent.[12] As has been stated, a considerable portion of the pigment accumulates at the oil-water interface, and hence flocculation is possible. The aggregates of pigment particles will tend to interlock and greatly increase the resistance of the system to shearing stresses, so that the viscosity of the emulsion, which is already high, will be further increased by the structure of the flocculates.

Bingham and Jacques[13] have found that the addition of a similar proportion of water to a lithopone paint results in a tremendous rise in yield value and a sharp decrease in its mobility. That the two cases, one in varnishes and the other in paints, are related, seems unquestionable. Gardner[14] shows the complexity of the problem when he refers to the beneficial effects in preventing "livering" sometimes obtained by the presence of large quantities of free acid and water in paints. The miscibility of water with the constituents of the varnish or paint will determine to a large degree the tendency towards emulsification. Work on the effect of moisture on both paints and varnishes is now being carried on in several laboratories.

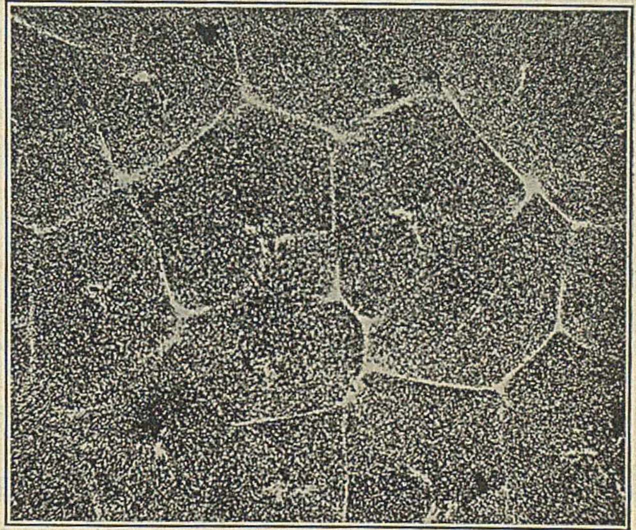

Figure 5 × 150

Conclusion

This discussion of the treatment of the defects of color varnishes has necessarily been restricted to generalizations. In practically every instance any or all of several different causes may function in the case of a given defect, and those directly responsible may be isolated only by individual treatment. Details concerning actual experimental work have not been given, because in almost every case the remedy discovered was specific and useful only for one particular varnish.

For example, ultramarine blue and carbon black varnishes show wide variations when suspended in the same volatile oils or varnish bodies. Flocculation is particularly annoying with carbon blacks, but not nearly so troublesome in the case of ultramarine blues. A sample of ultramarine blue varnish which originally celled very badly smoothed out into a beautiful uniform film when treated with a small amount of nitrobenzene. But when this same volatile was added even to a good carbon black varnish the results were most disappointing. The pigment, which was originally well dispersed, drew up sharply into broad lines, which ran in various directions through the film (Figure 6), though preponderantly parallel to the line of flow. The addition of the nitrobenzene seems to have decreased sharply the wettability of the carbon black toward the oil body. The piling up of the

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[12] Green, This Journal, 15, 122 (1923).

[13] This Journal, 15, 1033 (1923).

[14] *Drugs, Oils, Paints*, 35, 290 (1919–20).

pigment produces a dull, serrated film, which flakes readily and is worthless for ordinary use. Such variations in the behavior of the two pigments are frequently encountered.

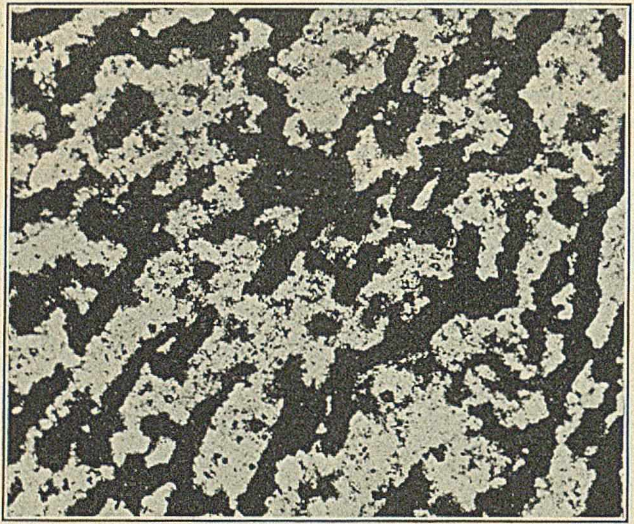

Figure 6 × 150

Thus each defective varnish, made according to its own formula from a given batch of raw material, which may differ widely from other lots of the same material, presents its own problem in determining a remedy. It is common experience in varnish mixing to find that two batches of varnish, made up according to the same formula, differ markedly in the quality of the product secured, simply because of minute variations in the physical and chemical properties of the ingredients.

It is impossible to offer a universal remedy for the various defects. It is usually difficult to trace any one defect to the fundamental cause, because of the inability to obtain a complete history of the methods of preparation of all the ingredients. Small variations in the methods of preparation may produce radical changes in wettabilities, adsorptive tendencies, etc.

As a rule, a microscopic examination of a drying film of any varnish is a dependable guide in the determination of its qualities. On such examinations and observations these papers have been largely based. The writers have considered principally the functions of the volatile and of the vortex action which it produces. A thorough comprehension of the relation of vortex action to the drying of varnish films seems to be fundamental to an investigation of the various defects encountered.

Hazards in the Handling and Transportation of Acid[1]

The Safety Factor

By Maurice F. Crass

The Grasselli Chemical Co., Cleveland, Ohio

All lines of industry have their package and transportation problems. The difficulties involved are intensified where the products constitute a hazard to handlers and merchandise in case of breakage or rupture of the packages. The ignorance or carelessness commonly displayed in the handling of acid is in no small degree responsible for the safety rating given acid containers, which rating would be greatly improved if all who handle these packages used methods best calculated to give the maximum of safety and efficiency. Malpractice in this respect is not confined exclusively to the transportation and consuming agencies. Recent surveys have shown the necessity for a close coöperative policy between producers and users of acid.

Acids most commonly used, such as sulfuric (including electrolyte or battery acid), muriatic, and nitric are rated by the Bureau of Explosives under the "Dangerous Article" class and are therefore accepted for transportation only (Interstate and Intrastate Commerce) when in compliance with the Interstate Commerce Commission's regulations. The policy followed by the Bureau of Explosives in drafting specifications—that of committee surveys in which the industry has opportunity to make suggestions and corrections—has improved conditions to such a degree that the proportionate losses incident to transportation are less than for many products not included in the "Dangerous Article" class. The coöperation of producers, transportation agencies, and consumers must continue if best possible results in reducing losses and safety in handling are to be attained.

Packages used for the transportation of acids must combine carrying strength, adaptability, ease of filling and discharge, with a type of construction best suited to withstand the action of the acid. A container that will serve for one acid may not be suitable for another. For this reason acid containers are specially constructed for the service intended. This is one of the chief reasons why the regulations are so specific. The type of construction is usually expensive, both in first cost and maintenance, and only possible to maintain because of the returnable feature which amortizes the cost over a tonnage otherwise prohibitive.

Generally speaking, the following materials are considered most efficient carrying agents—erosion, contamination of product, and strength of construction considered for the finished container:

Sulfuric Acid	Boxed glass carboys: See I. C. C. Spec. 1 Steel drums of 55- and 110-gallon capacity: See I. C. C. Spec. 5-A Steel tank cars: See American Railway Assoc. and I. C. C. regulations
Hydrochloric Acid	Boxed glass carboys Transportation tanks: wood, stave treated or rubber lined. Steel shell, rubber lined Steel drums: soft rubber lined
Nitric Acid	Boxed glass carboys with incombustible packing: See I. C. C. Spec. 1 Special steel drums: used only for acid containing certain maximum limitations on lower oxides of nitrogen, hydrochloric, and sulfuric with a minimum per cent of HNO_3
Mixed Acid	Steel drums and steel tank cars: same regulations as apply to sulfuric acid
Acetic Acid (including glacial)	Transportation tanks: wood stave construction, paraffin treated Hardwood barrels: paraffined Boxed glass carboys *Note*—Glass carboys are best suited for glacial, because of danger of discoloration of product when shipped in barrels
Aqua Ammonia	Steel drums: well seasoned Steel tank cars: well seasoned Boxed glass carboys
C. P. Ammonia	Steel drums: well seasoned Boxed glass carboys 5 and 1 pint glass-stoppered bottles in packed cases

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[1] Received May 14, 1925.

A brief historical review of the development of a few chemical packages will give a better understanding of the necessity for the restrictions imposed by the American Railway Association and Interstate Commerce Commission.

Carboys

The well-conditioned carboy cannot be considered as a fragile container, although there are definite limits to its shock-resisting strength. A broken carboy enroute means possible damage to merchandise, as well as danger to workmen who may not be informed as to the proper method of dealing with such leakage. The insistence, therefore, has been for a stronger, better-conditioned carboy and regulations that would eliminate the unfit.

A study of the problem was undertaken by a committee of representatives from the Manufacturing Chemists' Association of the United States and the Bureau of Explosives. The preliminary survey disclosed ample cause for complaints made by the railroads, who had suffered undue losses from broken and defective carboys. Regulations governing shock-resisting strength, standardization of construction, and maintenance were so general and unscientific that very little, if any, benefit was derived therefrom.

Certain dropping and side strain tests were prescribed, but the methods were in many cases so crude that the tests were of little value. The committee, therefore, devoted much time, pains, and money in determining: (1) a machine that would give an approximately perfect swing strain test; (2) reasonable strain test requirements; and (3) regulations governing conditioning of carboys, perfecting of seals, etc.

With a standardized swing testing machine, it became necessary to determine the minimum shock to which carboys should be subjected. This was a difficult matter, for it was necessary to consider (1) the elimination of a large number of carboys then in circulation, which were not equal in strength to other better constructed or better conditioned types; and (2) the reasonable average strain to which these better conditioned types should be subjected.

In approaching this problem the committee gave earnest consideration to what constituted a reasonable shock in transit and, after placing this tentatively at a collision shock speed of 8 miles per hour, equalized this by means of careful tests to the shocks transmitted by the shock testing machine and thus arrived at the 55-inch component now required in the regulations. The wisdom of this action has been shown by (1) the almost immediate effect on the industry in spurring the development of better conditioned and improved carboys; and (2) a reduction in damage losses to railroads by more than 50 per cent for the first year and a further large reduction the second year—a result rather astonishing when it is considered that considerable numbers of substandard carboys were still in service.

Further improvement was made through betterments in sealing practice. The old method of sealing a carboy by means of a vitrified stopper, covered over with plastic clay or plaster, burlap-wrapped and string-tied, was a practice productive of accidents and damage loss. This was remedied by developing and prescribing:

(1) A porous earthenware stopper, hard-burned and impervious to the action of acid—spillage proof and yet sufficiently porous to vent any pressure which might be otherwise built up in the bottle.

(2) A gasket made of treated (paraffin and oil) asbestos wicking—proof against the action of the acid.

(3) Metallic seals easily applied and not readily destroyed through gas or acid contact.

(4) A lip surfacing machine for repairing or surfacing away depressions in the lips of carboys chipped during course of service. The development of this machine made possible regulations forbidding use of chipped lipped carboys for transportation service.

The I. C. C. regulations further provide for semiannual tests on each type of carboy used for transportation service, one of which is made by an inspector of the Bureau of Explosives.

All users of acid in carboys should observe the regulation providing for the *complete emptying* of carboys before their presentation to the carrier for return. More accidents occur through spillage of acid on workmen from supposedly empty carboys than from all other causes in their handling. A safe practice is to flush the empty carboys with water and drain them thoroughly.

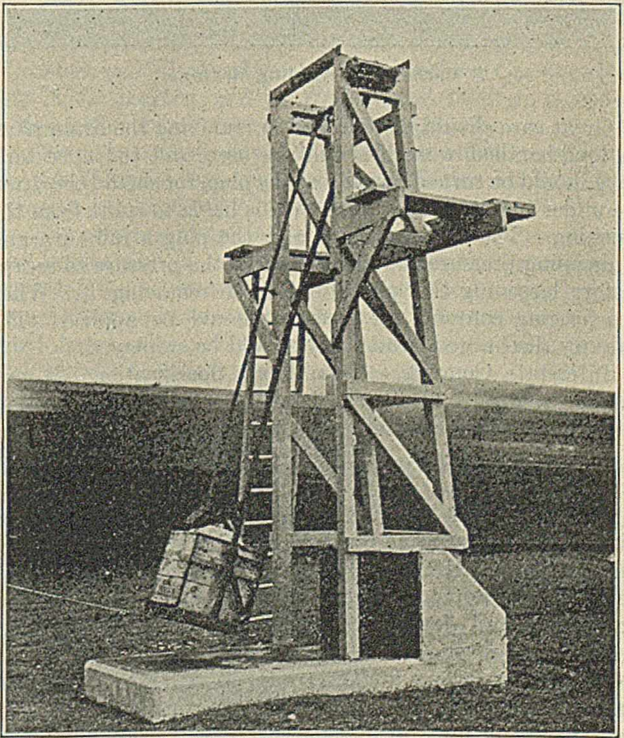
Carboys loaded in cars for return should be loaded solidly and should be well braced to prevent shifting. Adequate bracing is cheaper than broken carboys. Furthermore, empty carboys should never be loaded on their sides with the necks butting against the bottom of carboys in next row.

Drums

This package would seem to be an ideal one for the safe transportation of sulfuric and mixed (nitrating) acids. Various conditions, however, must be taken into consideration:

(1) The metal must be of sufficient gage to withstand severe transportation and dropping strains, with a margin of safety to care for deterioration during service.

(2) The welded seams must be free from carbonized or oxidized spots, for unless these are 100 per cent perfect the acid will search out the defect.



Carboy Testing Machine

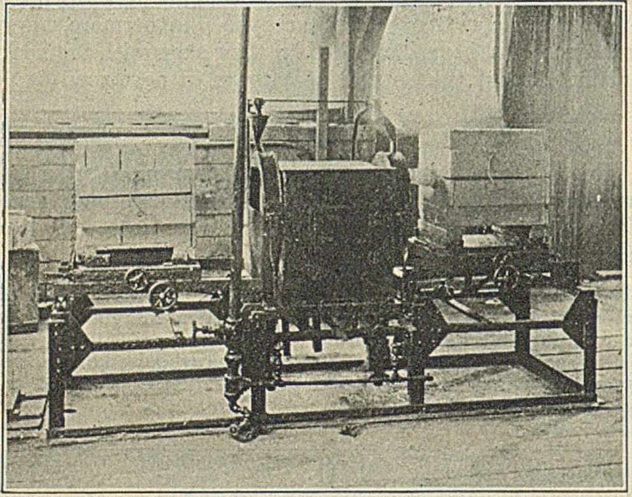
(3) The inspection and testing service before filling should be efficient and carefully supervised. Inspected drums only should be filled.

(4) Drum plug should be seated on a gasket made of asbestos rope wicking.

(5) Repairs should not be made on a drum until it has been thoroughly washed out with a soda ash solution or some other neutralizing agent. Even with this precaution there is possible danger from hydrogen gas; when making repairs an open flame should be used with the utmost caution, if at all.

Drums cannot be used with safety for transporting the weaker strengths of sulfuric acid. The Interstate Commerce Commission regulations place the minimum at 65° Bé. 60° F. This minimum was arrived at after careful tests showed that erosion of the steel took place very slowly in the presence of the higher concentrated strengths of acid, whereas below the minimum set the erosion was increasingly rapid with reductions in acidity.

All users of drums should scrupulously observe the rule of storing filled drums in a cool place, not exposed to the direct rays of the sun. Acid is volatile; liquids of any sort expand under increase of temperature. Full drums in stock should be stored with the plugs up. Internal pressure can be avoided by loosening the plugs occasionally.



Carboy Lip Grinding Machine

Great care should be exercised in removing the drum plug. A long-handled wrench should be used and the operator's face should be turned away from the plug, for should the drum be under "built up" pressure, acid is liable to spurt from the opening. The safe way is to give the plug a full turn and if escaping pressure is apparent, allow the pressure to escape before loosening the plug further or removing it. When discharging contents no pressure should be applied. The gravity discharge method only should be employed.

Interstate Commerce Commission Specification 5-A prescribes the gage of metal, detail of construction, testing, etc., under which conditions this package can be legally used.

Acid Tank Cars (Sulfuric and Mixed Acid)

This equipment is fairly well standardized. The construction of the underframe must conform to American Railway Association regulations. The design of dome, type of fittings, and other equipment detail vary to suit the individual experience and development. Certain procedure must be followed however, one requirement being a safety vent, attached to the dome fittings, equipped with a frangible disk, calculated to rupture at a pressure of 30 pounds. This takes care of "built-up" or internal pressure which may occur through rises in temperature, which expands the acid. An air cushion to provide for this expansion consists of a dome capacity equal to 2 per cent of the total capacity of the tank. No tank car should at any time be filled with acid level higher than the base of the dome.

Ordinary precautions should not be dispensed with when connecting up for the discharge of the tank. A small pressure (under the 30-pound rupture point of disk) may be present and this should be relieved by opening the air valve, the workman should protect his face and eyes against possible vapor when removing the cap or opening the valve on the acid discharge pipe fitting. Care should be taken to see that the fittings to the discharge line are in good order and the coupling pulled up tightly; otherwise spurting of acid might occur when pressure is applied to discharge the tank. Substitution of rubber hose connections for steel fittings in connecting up the tank with the acid discharge line is bad practice and should not be permitted.

A recent survey of tank-unloading practice by large consumers of acid disclosed serious violations of the instructions stenciled on the domes of the tanks. A maximum of 30 pounds air pressure is permitted, which is sufficient to discharge the acid to a height of approximately 28 feet. Tank cars were found connected up with air mains under 100 pounds pressure with no reducing valve control. Such practice is dangerous and should not be permitted. Where conditions necessitate transferring acid long distances or to elevations requiring in excess of 30 pounds air pressure to discharge, pumping should be resorted to. The tanks on tank cars are containers and transportation units, not blowcases, and they should never be used as such.

There is danger that the hydrostatic strain test as stenciled on the equipment be taken as indicative of the pressure that can be exerted in discharge operations. No one conversant with the testing and maintenance of boilers or other pressure equipment would consider operating such a unit under working pressures equal to those exerted under special tests. A safety factor of 2 to 1 is not excessive; therefore, the stenciling on the domes of tank cars limiting pressure for discharge to 30 pounds. That this practice has been wise has been demonstrated by the infrequency of acid leakage in transit and the rarity of cases where the tank or dome has "let go." In the few cases which have come under observation, the damage was caused by the excessive pressures exerted.

Dry air should be used in blowing because of the effect of moisture on the interior of the dome and shell. It is good practice to blow out the air line before connecting up. Naked lights should never be used around the dome of a tank car, whether loaded or empty. There may be hydrogen gas present.

All filled tank cars are protected in the course of transportation by the White Acid Label, as required by the Bureau of Explosives under the authority of the Interstate Commerce Commission. The presence of this label makes it the duty of all railroad employees to exercise unusual care in handling the car. It also places an obligation on receivers of this equipment to remove these labels as soon as the tank car has been discharged.

Orders from the trade calling for a definite tonnage less than the capacity of a tank car sometimes give rise to a dangerous practice—that of partially filling the tank. This should never be done; the movement of the acid under end shocks in course of transit puts the tank under an unnecessary strain and may damage the tank or shift it from its anchorage.

The care used in washing a tank has a direct bearing on its life. The introduction of water develops heat, forms a dilute, sour solution, which acts readily on the shell. This can be considerably reduced by introducing slaked lime or soda ash early in the washing. The regulations provide for the testing of tanks by either water or acid; in the latter case the dome is filled with acid, and when the test is complete, by siphoning out the acid in the dome, it is ready for the road. This reduces the washings necessary and adds to the life of the shell.

According to the Bureau of Mines, the production of sodium compounds, not including common salt, from natural salines and brines in the United States in 1924 amounted to 76,420 short tons.

Chlorine in Sewage and Waste Disposal[1]

By J. C. Baker

Wallace & Tiernan Co., Inc., Newark, N. J.

During the early development of a community the problem of disposal of human waste is very simple because it is scattered widely and nature rapidly disposes of it. The increase of population in certain areas, however, has been accompanied by methods of handling sewage which result in it being so collected at certain places that the problem has become increasingly difficult.

In China there are very highly congested areas in which these problems do not exist because of their economic system of waste disposal. The wastes are carefully saved and removed from the cities every night by those interested in agriculture who pay for the privilege of obtaining them for fertilizer. However, the Chinaman has paid the penalty for using human wastes for fertilizers, as all food or drinking materials which come in contact with the land must be cooked before being eaten. The national habit of tea drinking is partly accounted for by the safety to health gained from heating the water.

The principal method of sewage disposal in use in this country today consists in discharging the sewage into a body of water of sufficient size that the dissolved oxygen contained in the water can supply the biological demand of the sewage. This method does not destroy disease organisms and has resulted in the pollution of most of our streams and lakes, which constitutes a great menace to public health. Further methods of treatment include (1) simple screening of the solids and allowing the remainder of the sewage to discharge into a body of water; (2) the aërobic methods, as in the activated sludge or in the modern filter bed; and (3) anaërobic methods as in the septic tank or the Imhoff tank. Chemical precipitation with lime is also used to some extent.

All these methods, although they relieve the oxygen demand of sewage, still leave sludge or effluent which contains organisms dangerous to health. In order to avoid this menace the method of chlorination of water and of sewage has been developed. Chlorine is the best safeguard against the spread of intestinal and water-borne diseases known at the present time.

History of Sewage Chlorination

Probably the earliest attempt at using chlorine compounds in the treatment of sewage was made in England.[2] As early as 1854 the value of calcium hypochlorite was recognized by an English water commission. Javelle water has been used in France for over a century and has commonly been used elsewhere to treat small amounts of wastes. Electrolyzed sea water, known as Hermite fluid, was used in 1889 in England. In 1893 Wolf, in this country, electrolyzed strong salt solutions, which he called Electrozone, and treated the sewage from certain homes in Brewster, N. Y., to protect the Croton Lake water supply.

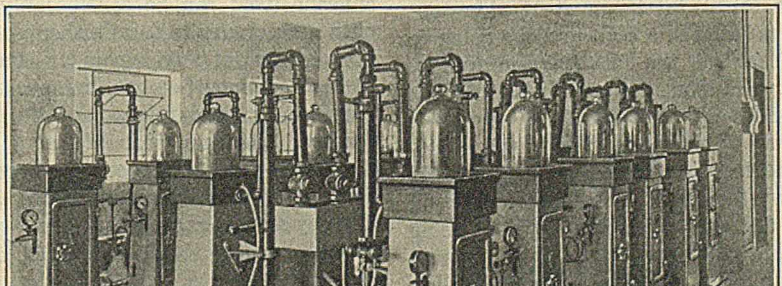
These attempts were all preliminary in nature and did not lead to the present widespread application of chlorine to water as a protective agent. The treatment of sewage was investigated by Earl B. Phelps, who determined the dosages required, the contact period necessary, the effects of temperature and organic content on the treatment, and developed a method of control by the use of starch iodide or *o*-tolidine and proposed a theory of sterilization. A similar investigation was conducted in England in 1904–5 by A. C. Houston.

The first commercially successful attempt at chlorination of a water supply was made by George Johnson in 1908 at the Bubbly Creek Filter Plant of the Union Stock Yards at Chicago. This work was quickly followed by others and in three years almost a billion gallons of water daily were being treated with calcium hypochlorite.

In 1910 Major Darnell, of the U. S. Army, demonstrated the value of liquid chlorine for the sterilization of water. His work was rapidly followed by that of others, particularly Ornstein and Kienle of the Electro Bleaching Gas Company, by D. D. Jackson, and by Wallace and Tiernan, in coöperation with various cities and water companies.

The chlorination of water supplies extended rapidly and liquid chlorine soon replaced hypochlorite because of its greater convenience, reliability, and accuracy.

The growing appreciation by health authorities that the contamination of water supplies must be prevented by treating the contamination at its source has recently caused much increase in sewage chlorination. The process is only in its infancy and experiments and developments are in progress which will doubtless greatly extend this use of chlorine.



The Largest Chlorinating Installation in the World at the Easterly Sewage Disposal Plant, Cleveland. Capacity 6.5 Tons of Chlorine Daily

Methods

Chlorine has been applied in many forms: as calcium hypochlorite from bleaching powder or from combination of gaseous chlorine with aqueous suspensions of hydrated lime; as sodium hypochlorite from electrolyzed sea water or electrolyzed brine, from the reaction of bleaching powder and soda ash solutions, from chlorinated soda ash and from chlorinated caustic. The application as a gas has been from chlorine generated from electrolytic cells, chlorine gener-

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[1] Presented before the Western New York Section of the American Chemical Society, Niagara Falls, N. Y., February 10, 1925.

[2] See Race, "Chlorination;" Hooker, "Chloride of Lime in Sanitation," for complete references and history of chlorination.

ated by chemical methods as by manganese dioxide and acid and salt and from gas liquefied in cylinders. It has been applied to sewage directly as a gas and as an aqueous solution.

Chlorine has also been applied experimentally as magnesium hypochlorite, as hypochlorous acid, and in combination with ammonium compounds such as nitrogen trichloride and as chloramine. Of these methods the most promising for future use is compressed chlorine from cylinders for large requirements and sodium hypochlorite where small amounts of chlorine are required and where the presence of compressed chlorine is undesirable. Chlorine can be applied to sewage at any place in which it can be contacted with the sewage from its raw state to any stage in the process of purification except in the chambers where biological action is going on. If used at this stage it would stop the biological action and interfere with the disposal method. However, the chlorine is almost invariably applied to the effluent from the process because less chlorine is required. In case chlorine is applied directly to raw sewage it is always desirable to screen the sewage and remove the large particles which are difficult to penetrate and sterilize. If possible, sewage should not be allowed to become septic before treatment, as this increases the amount of chlorine required.

Domestic sewage requires usually somewhere between 3 and 20 parts per million, depending upon its concentration and condition. Usually domestic sewage can be satisfactorily treated with from 5 to 10 parts per million of chlorine to give a 95 to 99 per cent reduction in bacterial count.

Applications

There are reasons for the chlorination of sewage other than to protect public health. Tannery wastes are chlorinated to protect cattle from anthrax. Large amounts of chlorine are necessary, 250 parts per million being required to kill the spore-forming anthrax in the presence of the large amounts of organic materials in tannery waste.

Chlorine is being used to protect bathing beaches. The Surgeon General of the U. S. Army says that "bathing pool water is, to all intents and purposes, drinking water and must, in general, conform, with the same sanitary standards." Many swimming pools are now being chlorinated to protect public health.

Most of the sewage in the city of Cleveland during the bathing season is treated with chlorine to protect the bathing beaches of the lake. These installations of equipment are the largest in the world for the handling of chlorine for sterilization purposes. In the Tidal Basin at Washington, D. C., a chlorinator was mounted in a boat and the chlorine distributed through the basin as the boat traveled around. Very fine results were obtained from the use of this method.

Protection of food supplies by chlorination of sewage is a growing and promising use of chlorine. The oyster industry is already widely protected by the treatment of sewage which may contaminate oyster beds. A further protection of the oyster supply by the use of chlorine is now being contemplated. Two methods are proposed: first, to treat the shelled oysters with sufficient chlorine water to sterilize the containing liquid; and, second, to immerse the unshelled oyster in strong chlorine water, which exhausts itself by reaction on the organic material on the outside of the shells and renders everything outside of the oyster sterile. As soon as the chlorine has been absorbed the oyster opens the shell and starts to circulate water through his respiration system. The circulation of sterile water by the oyster will, it is claimed, in the course of 6 hours completely eliminate any contaminating organisms within the oyster. By giving two successive treatments oysters can be rendered satisfactory for use as food. Probably both of these methods of oyster treatment should be used to remove contamination within the oyster and to safeguard against contamination of the oysters during or after shelling.

A further use of chlorine in connection with food supplies is possible, though not practiced. Probably the greatest waste of a natural resource in our present civilization is the loss of human wastes as fertilizer. In certain regions of this country it should be possible for the sewage effluent from the cities to be returned to the land, and this effluent should be first rendered sterile by chlorination. Perhaps this generation will see this process in use.

Chlorine can also be used for the decolorization of industrial wastes so that these wastes can be discharged into streams without damaging the stream. This has been practiced for some time in isolated cases and is now coming into extended use in paper mills, textile and dye houses, and many other industrial plants who must discharge satisfactory waste liquors or remove their plants from the present location.

In those centers of population where the water receiving the sewage is overloaded and becoming septic produces objectionable odors, it is feasible to chlorinate the sewage discharging into such streams sufficiently to retard the biological action in the streams and permit the sewage to be swept out further into the larger bodies of water. This seems to be a feasible solution of the problem that will eventually develop in the Hudson River at New York City. It would be difficult to install modern sewage treatment plants in New York. If the sewage were chlorinated sufficiently to retard the biological action of the river, the capacity of the stream for handling sewage would be increased and the time delayed when increasing concentration of population would make the Hudson and East Rivers septic and damaging to the city's interests.

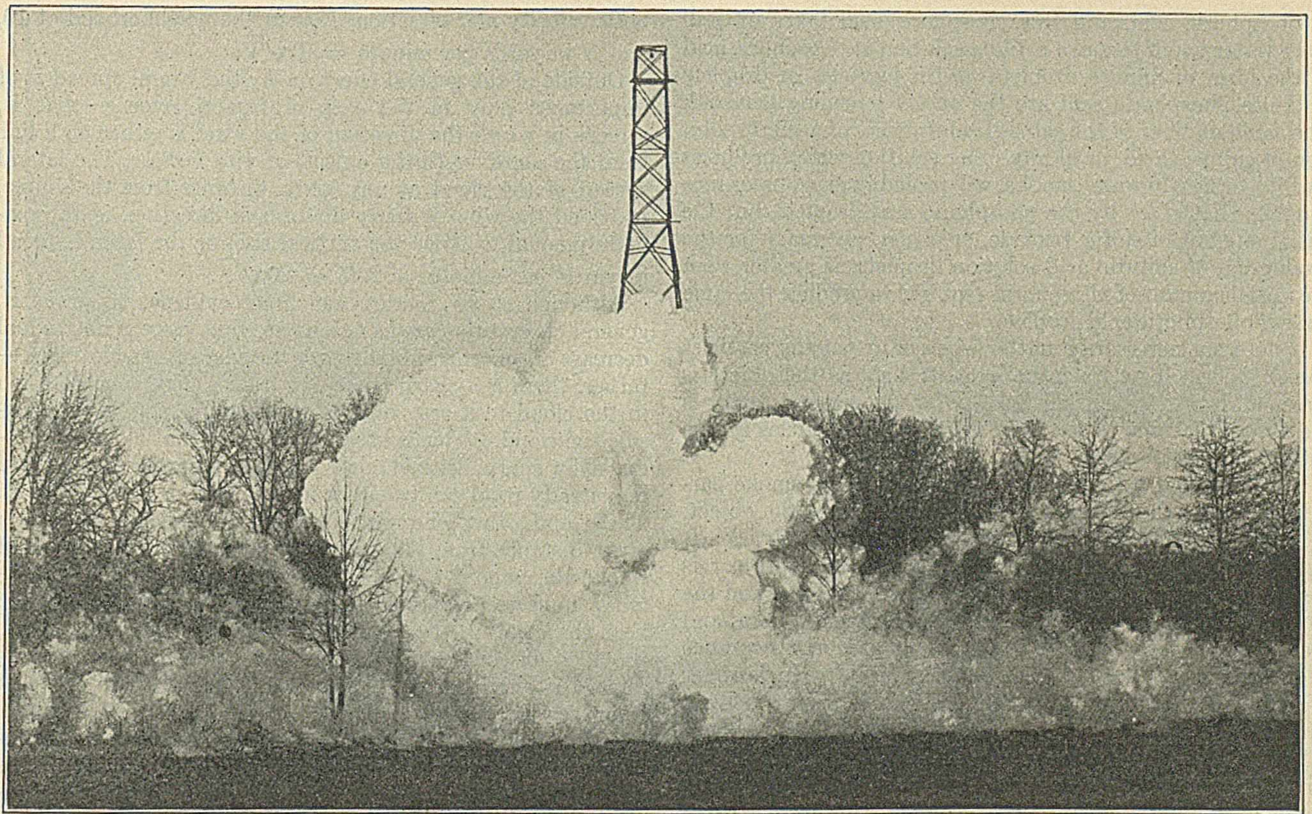
Chlorine is now being extensively used to deodorize the obnoxious gases being discharged from stacks, particularly those from garbage and fish reduction plants and packing houses. This use is only in its infancy.

Theory of Action of Chlorine

The manner in which chlorine acts in sterilizing water and sewage is of interest. The evidence is strongly in favor of the theory that the killing action is not due to direct oxidation by the chlorine but to the formation of some substance toxic to the organism. Substances of greater oxidizing potential than chlorine, such as permanganate or peroxide, need to be used in much greater equivalent amount than does chlorine to show similar sterilizing action. The oxidizing power of chlorine itself can be considerably reduced by combination with ammonium to form either nitrogen trichloride or chloramine, without any loss in its sterilizing capacity and very little alteration of its sterilizing rate, though the compounds, particularly chloramine, have a relatively low oxidizing potential. Chlorine probably acts by attacking the lipoid protein surface of the cellular organisms and forming there some substance which interferes with further cell division, thereby stopping regeneration and resulting in the death of the organisms.

Change in Motor Gasoline Specification

A tentative change in the specification for U. S. Government motor gasoline, the principal feature of which is the elimination of the initial and end point requirements, has been voted by the Technical Committee on Lubricants and Liquid Fuels of the Federal Specifications Board. The change, however, will not be immediately effective, as the committee feels that it is necessary first to purchase limited amounts of gasoline on the tentative specification for experimental test. In voting the tentative change, the committee believed that if the gasoline meets the present distillation requirements at the 20, 50, and 90 per cent points it should be satisfactory.



Smoke Cloud from 100-Pound White Phosphorus Airplane Drop Bomb

Screening Smokes[1,2]

By H. W. Walker

Chemical Warfare Service, Edgewood Arsenal, Md.

THE masking of movements of attacking troops is probably as old as the art of warfare. Taking advantage of natural cover or darkness to surprise the enemy, or to conceal the direction of an attack, was fundamental knowledge, even among savages. Artificial means of this kind date back at least as far as the use of the wooden horse at the siege of Troy. Shakespeare describes artificial masking of the advance of an army in "Macbeth," where "Great Birnam Wood moved to high Dunsiname Hill," each man cutting down the bough of a tree and carrying it before him to "shadow the numbers of our host, and make discovery err in report of us."

Smoke screens had been used to more or less advantage in minor naval operations at least as far back as the Civil War, when blockade runners, to evade pursuit, took advantage of dense black smoke produced by using wood high in pitch and resin as fuel for the boilers. But no large-scale intelligent use of screening smokes was made by military forces prior to the World War, when its importance, both as an offensive and a defensive factor, was definitely established.

Theoretical

Definition and Properties of Smoke Screens

A smoke screen consists of a cloud of liquid or solid particles in a very fine state of subdivision between the observer and the object in sufficient concentration to obscure the object completely from the observer.

The screening effect of different smoke materials is probably proportional to the quantity of material between the eye and the object, provided the materials are in the same relative state of subdivision and, if the term "volume" be substituted for "quantity," the screening effect is probably directly proportional to the total volume of all the particles between the eye and the object, regardless of the material, if it is assumed that the material is in the same state of subdivision. As a matter of fact, the bulk of visible particles which go to make up a smoke cloud are of the order of from 10^{-4} to 10^{-5} cm. in diameter, and under the average field conditions the particles could be considered of the same degree of subdivision without the probability of very great error.

Note—The blinding effect of light superimposed upon the eye by reflection from white clouds has always been supposed to make white smokes more effective than black smokes, but no quantitative data have been available on this point. Experiments are now under way which will determine quantitatively the relative efficiency of white, black, and intermediate colored smokes.

The material between the eye and the object is usually different in its chemical composition from the original compound in that it has combined with one or more of the constituents of the air. Thus, in the case of phosphorus, phosphorus pentoxide is formed first and then phosphoric acid, or in other words, one pound of phosphorus combines with the oxygen and water vapor from the air to produce 3.16 pounds

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[1] Received March 26, 1925.

[2] Published by permission of Chief, Chemical Warfare Service.

of phosphoric acid, and this phosphoric acid takes up still more water vapor to make a dilute solution of phosphoric acid in the form of minute droplets, which particles or droplets of dilute phosphoric acid are the actual screening material. The same number of the same-sized droplets of a dilute solution of sulfuric acid, or of any other solution which produces a white, or nearly white, smoke, will probably give obscurance equal to that given by the phosphoric acid droplets, but the initial amount of sulfur trioxide, or oleum, necessary for the production of sulfuric acid solution droplets, is greater than the initial amount of phosphorus required to produce the same bulk of phosphoric acid droplets.

It does not necessarily matter whether or not the particles absorb, reflect, or refract the light, so long as the object is screened, but it is believed that by far the greatest factor is the actual blocking of the light rays by the particles in line with the object.

It follows that if there is a sufficient volume of smoke particles between the eye and the object to obscure the object, it makes no difference whether this volume of particles is highly concentrated in a comparatively small depth, or is spread out along the entire distance between the eye and the object. This has been borne out by experimental data, and these data, in fact, indicate that possibly greater obscurance is obtained by spreading the same volume of particles over a greater depth than by confining them in comparatively narrow limits.

In the case of practically all substances being considered for military smoke screens, the particles of actual smoke-producing material are liquid. In the case of destroyer smoke screens used by the Navy, the actual smoke-producing material is probably a combination of liquid particles of oil and moisture and solid particles of finely divided carbon.

Cloud Travel

Inasmuch as smoke is carried with the wind, in order to screen any objective for a given period of time it is necessary to generate smoke continuously for the desired length of time from a source which may be either a point or a front. It naturally follows that it is necessary to understand the fundamental mathematics of smoke cloud travel. Observations of a great many clouds indicate that the resultant of the upper boundary of a smoke cloud is a straight line for at least the first 600 yards of its travel and the available data on longer clouds indicate that this straight line effect continues for practically the life of the cloud. It is true that there is a small initial rise in the first few yards, due to the initial thermal effect of smoke generation, but what evidence there is seems to prove that this effect is dissipated before the cloud has traveled a hundred yards. It is also true that the smoke cloud travels at approximately the same speed as the wind, and that the resultants of the lateral edges of the cloud may be considered straight lines. In other words, the cloud spreads more or less uniformly both upwards and sideways as it travels along. The main causes of this spread are the turbulence of the atmosphere and the character of the terrain. The turbulence of the atmosphere seems to be a function of the wind velocity, and it has been shown that for any given wind velocity the rise per minute of the cloud is approximately equal to a constant times the square root of the wind velocity in miles per hour, or $H = K\sqrt{V}$. This constant is really made up of two variables and a constant, the variables both being functions of the wind velocity. One, called the "gustiness" factor, is obtained by dividing the average wind velocity by the maximum variation of the velocity and adding one; the other is an arbitrary factor based on the changes in direction of the wind during the generation of the smoke cloud. If the wind is fairly steady in both velocity and direction, K is in the neighborhood of 10, and H in yards per minute $= 10\sqrt{V}$.

Outside of the general effect on K, the lateral spread is of importance only in the case of frontal screens—that is, screens in which the direction of the wind is either on a line from the observer to the object, or vice versa. The lateral spread of the cloud at any given distance from the source, provided the wind is fairly uniform in direction, is approximately equal to twice the vertical rise, or the lateral spread in yards per minute $= 2\,H = 20\sqrt{V}$.

Although so far there is no direct evidence to prove it, general observation seems to indicate that there is no gradual decrease of concentration towards the edge of a smoke cloud—rather, there is a sharp transition from a high concentration in the cloud to a zero concentration of the smoke just outside the cloud. This is based on the fact that clouds in general show sharp, distinct edges and that a person near a cloud in a steady wind can be either in the cloud or just outside it. These and other observations seem to indicate that at a given distance from the source the average concentration of smoke throughout a cloud generated from a single source is fairly uniform, regardless of whether the sample is taken near the edge, in the middle, or near the top of the cloud, provided, of course, that the distance from the source is the same. It is hoped in the near future definitely to prove or disprove this assumption by actual analysis of samples. It is evident from the foregoing that the decrease in concentration or density of a smoke cloud is proportional to the square of the distance or $C = K/D^2$, where C is the concentration, K a constant, and D the distance from the source in yards.

In addition to the concentration data desired above, it is hoped that analysis of samples of various smoke materials will give an exact idea of the amounts of water vapor that are taken up from the air by various smoke agents under varying conditions.

Properties of Ideal Smoke-Producing Material

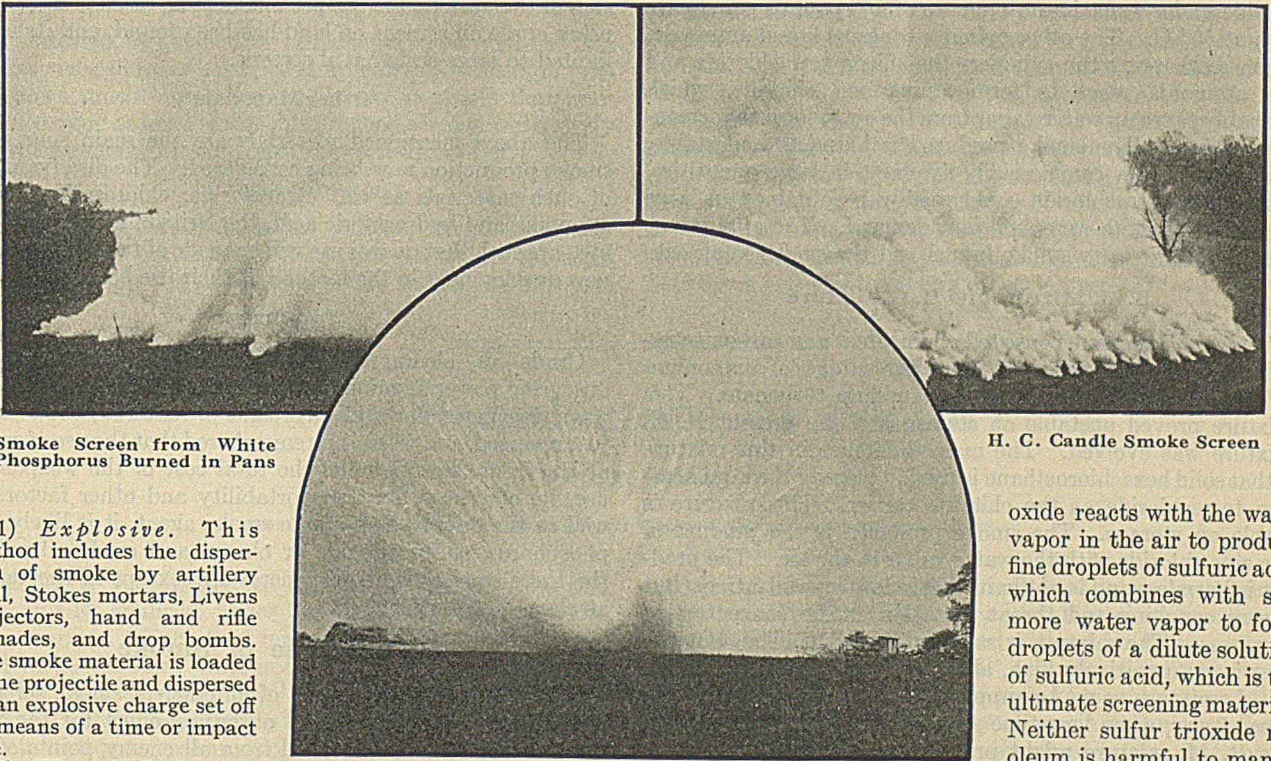
The ideal agent for screening smokes should produce a maximum volume of actual screening material for a minimum original weight. Its characteristics should be such that the rate of smoke production can be readily controlled, and little or no heat should be evolved in the formation of the final obscuring product. It should be nontoxic and nonirritating. It is obvious that it should be readily available and commercially economical, and should not be dangerous to handle.

If it were possible and practical, probably the ideal smoke screen would be one in which the cloud was manufactured by the catalytic change of the water vapor in the air to particulate droplets, especially if a mobile catalyst could be devised which could perform this phenomenon in any particularly desired area or locality. Failing this, if a method could be devised for the catalytic oxidation and synthesis of sulfur to minute droplets of a dilute solution of sulfuric acid, using the oxygen and water vapor of the air, it would probably be a more economical and practical smoke than white phosphorus.

The possible atomization of water into minute droplets of between 10^{-4} and 10^{-5} cm. in diameter, by forcing through a nozzle or by any other means, might produce screens very economically and efficiently.

Methods of Smoke Generation

There are three general classes of dispersion, all of which are used to some extent in the production of screening smokes, and require chemical or physical change before the final obscuring product is formed:



Smoke Screen from White Phosphorus Burned in Pans

H. C. Candle Smoke Screen

Cloud from Burst of 4-Inch White Phosphorus Stokes Shell

(1) *Explosive.* This method includes the dispersion of smoke by artillery shell, Stokes mortars, Livens projectors, hand and rifle grenades, and drop bombs. The smoke material is loaded in the projectile and dispersed by an explosive charge set off by means of a time or impact fuse.

(2) *Thermal.* In this class is included the production of smoke screens by means of candles, airplane exhaust, smoke boxes, the stacks of destroyers, etc. The general principle is that the original material is converted by means of heat into a form whereby it acts chemically and physically with the constituents of the air to produce the final obscuring product.

(3) *Pressure.* This method of smoke production includes the use of oleum, titanium tetrachloride, and tin tetrachloride released from cylinders, the navy smoke funnel, and similar appliances. Usually the agent is placed in the cylinder under pressure and upon being released through an atomizing nozzle passes through the vapor phase and is condensed in the form of small particles, which react with the constituents of the air to a greater or less degree, depending upon the specific properties of the material. In the case of the navy smoke funnel type, two materials are stored in cylinders under pressure and released simultaneously to combine chemically to form a compound which reacts with the constituents of the air to form the final obscuring product.

Present Materials Considered for Screening Smokes

White Phosphorus

White phosphorus is a solid, melting at 44° C. and boiling at 290° C., which oxidizes upon contact with air at ordinary temperatures, or upon burning in air, to form phosphorus pentoxide, which takes up water vapor to form phosphoric acid, and this phosphoric acid absorbs still more water vapor from the air to form a dilute solution of phosphoric acid. One pound of phosphorus produces 3.16 pounds of phosphoric acid. It is commercially available in large quantities and is comparatively reasonable in price. It is used in shell, Stokes bombs, grenades, drop bombs, and attempts are being made to use it in a candle. It is not corrosive when sealed in iron or steel containers, and the smoke produced under field conditions is not injurious to men or equipment.

Sulfur Trioxide and Oleum

Oleum is a solution of sulfur trioxide in sulfuric acid. Sulfur trioxide exists in two forms, the ordinary stable one which would be used for chemical warfare work being the beta modification, which melts at 50° C. The sulfur trioxide reacts with the water vapor in the air to produce fine droplets of sulfuric acid, which combines with still more water vapor to form droplets of a dilute solution of sulfuric acid, which is the ultimate screening material. Neither sulfur trioxide nor oleum is harmful to man in ordinary concentrations—although they are somewhat irritating—and both are readily available on a large scale commercially, can be stored in iron or steel containers, and are economical in price. The only use for pure sulfur trioxide is in shell or bombs, but oleum can also be used as a spray in the exhaust of airplanes—although it is quite injurious to the present airplane fabric—in tanks and destroyers, and may possibly be used in airplane curtains.

Titanium Tetrachloride

This material is a liquid boiling at 136° C., which, when released under pressure through a nozzle, forms a a hydrate, $TiCl_4.5H_2O$, with the water vapor in the air, which upon further reaction with moisture breaks up into titanium hydroxide and hydrochloric acid. Under conditions of high humidity this hydrochloric acid condenses with water to form minute droplets of dilute hydrochloric acid solution. Titanium tetrachloride smokes dissipate more quickly than either phosphorus or oleum smokes, even under conditions of high humidity, possibly due to the difference in vapor pressure of solutions of hydrochloric acid as compared with phosphoric acid or sulfuric acid. The smoke produced is not injurious to man under ordinary conditions, and is only slightly irritating. The liquid titanium tetrachloride is corrosive to fabrics and the human skin, and is highly injurious to untreated airplane fabric. Titanium tetrachloride is not now available in large quantities commercially and is comparatively expensive. Although the smoke is considerably inferior to white phosphorus or oleum in shell and bombs, it is used at present in the airplane exhaust smoke and the airplane curtain because it is the most desirable for that purpose.

Silicon Tetrachloride, Ammonia, and Water

The proportions that give the best results are 2 of silicon tetrachloride to 1 of ammonia by weight. This smoke is generated from a smoke funnel. One cylinder is charged with silicon tetrachloride containing about 10 per cent carbon dioxide under a maximum pressure of 550 pounds per square inch at 55° C. The other cylinder contains liquid ammonia. Upon discharging the cylinders the silicon tetrachloride and the ammonia react to form ammonium chloride, which probably takes up water vapor from the air to form the screening product. The smoke produced is harmless and stable. Ammonia is now commercially available in large quantities, and silicon tetrachloride could readily be obtained in large quantities if there were sufficient demand. These materials are used in the navy smoke funnel and the smoke knapsack.

B. M. Mixture and H. C. Mixture

The B. M. mixture consisted of zinc dust and carbon tetrachloride along with relatively small percentages of ammonium chloride, sodium chlorate, and magnesium carbonate. This mixture proved unstable on storage and the present H. C. mixture was evolved. The main difference in this mixture is that solid hexachloroethane is used in place of the liquid carbon tetrachloride as the chlorine carrier. This mixture is stable on storage. The smoke produced is the product of the zinc chloride with the water vapor in the air. The product is harmless and is not irritating in low concentrations, but causes coughing and throat irritation as the concentration increases. The mixture is safe and easily handled, but the cost is comparatively high, although either the H. C. or the B. M. mixture could be supplied on a large-scale basis. In case of war, when long-time storage would not be necessary, the B. M. mixture might prove more economical.

These mixtures are used in candles, the 4-inch Stokes mortar shell (burning type), and H. C. grenades.

Crude Oil

A dense, dark smoke screen can be set up by destroyers by spraying oil below the stack with an insufficient supply of air. The smoke itself probably consists of particles of carbon and some tarry and oily matter, augmented by films of condensed water vapor. This method of smoke production cuts down the speed of the destroyer and fouls the boiler tubes, but it is probably one of the most economical methods for the production of naval screens by destroyers. The smoke is harmless, but soils everything with which it comes in contact. The smoke-producing material is always available, being part of the fuel supply necessary for the propulsion of the vessel. At the present time no feasible method of using crude oil screens on land has been found, and its use is limited to large-scale naval screens.

Other Materials

The above-mentioned materials are the main sources of smoke production now being considered. The disadvantages of such materials as tin tetrachloride, chlorosulfonic acid, ammonia and hydrochloric acid, the British Type S mixture, etc., are such that no real use will be made of them unless some new development in the method of their use be discovered.

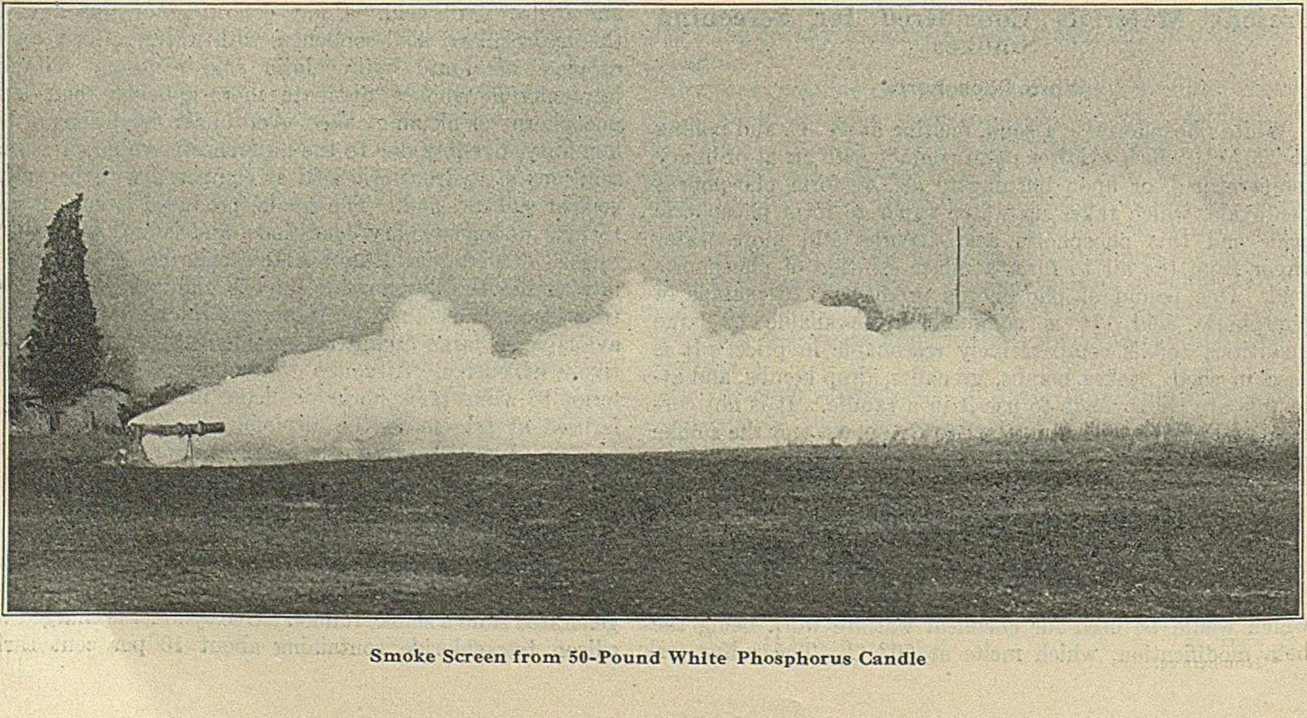
Summary

Crude oil, oleum, and phosphorus will give maximum obscuring power at minimum cost, in the order named. For obscuring power for a given weight of material, the order is just reversed, and when it is remembered that the use of smoke at the front depends upon the total cost of the weapon, its use, its efficiency, its transportability and other factors, as well as the original cost of the smoke agent, it is likely that phosphorus, sulfur trioxide or oleum, and crude oil will be the three smoke agents of general use, except in the case of airplane distribution.

Tactical Use of Smoke

Briefly stated, the essential of an efficient smoke screen is that it must give the desired obscuring effect for the total front or object to be screened from all enemy points of observation for the desired duration of the screen, with minimum impedance to one's own observation, artillery fire, and general communications.

This necessitates a thorough knowledge of all phases of the situation by the gas officer, who must determine whether or not these conditions can be met by use of the material on hand under the prevailing weather conditions. Knowing the kind and quantity of smoke agents on hand, and the weather conditions, he should be able to determine how large and how effective a screen can be established at a given locality, and how long it can be maintained. It naturally follows that he must make the choice of method for establishing and maintaining the screen and, according to the situation, should decide whether artillery, Stokes, Livens, candles, airplanes, or other devices should be used.



Smoke Screen from 50-Pound White Phosphorus Candle

Airplane Possibilities

The development of the airplane exhaust and curtain smokes since the war has opened up new possibilities in putting down much more effective screens at points that were hitherto more or less inaccessible for good screens and a study of airplane smoke tactics constitutes a field in itself.

Naval Possibilities

Especially is this so in naval warfare, where previously screens had to be maintained by the use of an excessive amount of smoke for a very long period to enable destroyers to attack successfully. By use of airplanes, effective and economical screens can be established for any desired sea area, and the screen can be originated comparatively close to the target or object, instead of five miles or more away, as was previously necessary. In addition to screening torpedo attacks by destroyers, these screens can be used to block out part of the enemy fleet, making possible a concentration of fire on almost any desired number of enemy ships at a cost of very little material, and the probability of loss of airplanes would be much less than the probability of loss of one or more destroyers engaged in setting up such a screen.

The Manufacture of Pectin[1]

By C. P. Wilson

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PECTIN was discovered in 1825 by Braçonnot,[2,*] who made artificial jellies with pectin obtained from carrots. Since then many chemists have been interested in pectin from various standpoints. A study of the splendid work of Fellenberg[15] with its accompanying bibliography brings one about up to the date of that publication in his knowledge of pectin, though Ehrlich[14] attacks the question of the chemical constitution of pectin in a fundamental way and makes a distinct contribution to that subject. Many others have worked or are working on pectin, and the literature is increasing in volume and in value.

A brief review of patent and other literature bearing on the manufacture of pectin prefaces a discussion of the principles utilized in the recovery of this article. Raw materials are apple citrus and beet refuse pulp or carrots.

The production of pectin is followed through the several stages in its development, from the use of apple pectin stock to assist in jelling the juice of other fruits to the production of a dry pure pectin from citrus fruits by the application of principles of colloid chemistry.

Present Status of Pectin Work

The lack of standard nomenclature is recognized by everyone who studies pectin literature, and although there is now some tendency toward better agreement in this matter there is urgent need for absolute uniformity. Other great needs are for a knowledge of the actual chemical identity of pectin and a rapid accurate method for its determination.

There is disagreement as to the composition of the various pectin bodies, and Tutin[28,29,30] denies the existence of protopectin as the precursor of pectin as proposed by Tschirsch,[27] Sucharipa,[23] and others.

Function of Pectin in Jelly

Regardless of these differences of opinion as to the exact nature of pectin, or indeed as to whether pectin is a chemical individual or a family of substances, the name is generally accepted as meaning that thing occurring in fruit and other parts of plants by virtue of which, in combinations with proper amounts of sugar, acid, and water, fruit jellies acquire and maintain their consistency as jelly. The term "fruit jellies" is used in a general sense to cover also jams or any other fruit preparations that normally have the consistency of jelly whether they contain fruit pulp or only clear juice.

Although it is customary to boil fruit juices to obtain a proper concentration to produce a jelly, it has long been recognized that jellies can be produced without heat and we have household recipes for "sun jelly" or "cold jelly." Currants are the outstanding possibility for making cold-process jelly, as they normally contain plenty of pectin and acid without concentration of the juice, but other fruit juices can be used when the fruit is in just the right condition.

It was but natural that after the role of pectin in jelly-making was recognized attempts should be made to isolate this substance and by its use secure better control of the jelly-making process and eliminate the uncertainty or failure due to variation in different kinds of fruits or in the condition of fruit of the same variety.

Jelly Stock

Probably the first use of added pectin was by the housewife, when she learned that by mixing juice from cooked apples with the juice of berries she could make a firm jelly which could not be produced from the berry juice alone. From this the practice grew into the production of "stock," which was a pectin solution obtained by boiling apples, apple pomace or apple skins, cores, and trimmings, and straining off the liquid. This was the simplest method of extracting pectin. Boiling converted protopectin into pectin and the latter being soluble in the dilute solution of malic acid, there was obtained a solution of pectin that could be used to enrich juices deficient in this substance.

When adopted by the jelly manufacturers this practice was subject to gross abuse, and thousands of tons of jellies paraded under attractive labels indicating the presence of fruits which were either entirely absent or present in such small proportions that they gave no distinctive character to the product. This abuse was the initiator of its own correction. Thanks to the efforts at proper legislation and its enforcement, bad conditions are being corrected and the better element of the jelly-making business is actively interested in the proper use of pectin and in legal restrictions that will eliminate the abuses associated with it.

Attempts at the recovery of pectin and studies of its use in jelly-making have not been confined to commercial firms, but

[1] Presented as a part of the Symposium on Pectin before the joint meeting of the Divisions of Agricultural and Food Chemistry and of Biological Chemistry with the Division of Sugar Chemistry at the 70th Meeting of the American Chemical Society, Los Angeles, Calif., August 3 to 8, 1925.

[*] Numbers refer to bibliography at the end of article.

the federal[5,9,22,24] and some of the state governments and universities have expended considerable time and money on this problem.[4,7,8,16,17,25,26]

Early Manufacture

For many years commercial jelly-makers have made jelly stock from apples or, more often perhaps, from apple pomace or from the skins, cores, and trimmings left from the production of dried apples and other products of the fresh fruit. In this way a pectin solution of variable quality and doubtful keeping quality was obtained. Attempts were made to concentrate the pectin solution in open kettles with varying success and later vacuum concentration was developed. Finally, methods were developed for the separation of pectin from its solution by precipitation, drying, etc. The activity along this line has naturally resulted in the issue of a number of patents based on a variety of pectin preparations and a still greater variety of methods for obtaining them. The principles used in the various methods proposed will be outlined here.

Raw Materials

The principal sources of pectin so far suggested are apple pomace or the refuse from cider and vinegar mills, citrus peels or the refuse from the production of citric acid and other major citrus products, beet pulp or the residue from beet sugar manufacture, and carrots which can be raised quite cheaply. So far as is known only the refuse from operations handling apples or citrus fruits have been used commercially as sources of pectin.

The amounts of pectin in these raw materials are given in Table I.

Table I—Percentage of Pectin in Raw Materials

MATERIAL	Pectin in fresh material Per cent	Pectin on water-free basis Per cent
Apple pomace	1.5 to 2.5	15.0 to 18.0
Lemon pulp	2.5 to 4.0	30.0 to 35.0
Orange pulp	3.5 to 5.5	30.0 to 40.0
Beet pulp[14]	1.0	25.0 to 30.0
Carrots[31]	0.62	7.14

The percentage of pectin found in prepared products such as fruit or beet pulp or pomace depends on the processes to which it has been subjected. If cold-water extraction has leached out sugars, acids, etc., and excess water is removed by pressing, the pectin content remains relatively high, while hot water treatments, especially in acid solution, reduce the residual pectin.

Extraction Methods

Pectin is usually extracted from the raw material by means of warm or hot acid solutions. Of the organic acids, citric, tartaric, lactic, acetic, and malic have been specified by various workers, and some have preferred a mixture of two or three of these acids. Acetic has generally proved unsatisfactory. Of the inorganic acids hydrochloric, phosphoric, sulfurous, and sulfuric have been tried. In the work of this laboratory sulfurous acid has been found satisfactory.

Some have conducted the extraction under pressure,[17,21] but it is more usual to boil a short time at atmospheric pressure with a dilute acid. Douglas,[12] for instance, subjects the "fruit pulp to the action of hot or boiling water containing a small proportion of any suitable acid."

Huber[18] extracts with an alkaline medium containing 2 to 4 per cent sodium hydroxide for 15 to 30 minutes at 40° to 80° C. He does not get pure pectin, but sodium pectate, from which pectic acid is precipitated. A peptizing agent such as sodium or potassium citrate or tartrate is used to get the pectic acid in solution. This product has not been utilized commercially.

Beylik[1] extracts impurities from citrus peel with alcohol and leaves a mixture of pectin and cellulose fiber which can be used with the fruit, the fiber being strained out with the fruit pulp.

Purification of Extracts

Various methods of purifying pectin extracts are proposed. Some specify removal of sugar[13] or sugar and acid from the raw material by cold-water leaching, one removes starch[12] by means of a diastatic enzyme, and another removes protein[6] by means of a proteolytic enzyme. The object of the removal of starch and protein is to get a pectin that will make clear jellies.

Methods for Precipitation of Pectin

Four principles have been used in the processes for precipitating—viz., alcoholic precipitation, salting out, electrolytic precipitation, and colloidal precipitation.

Precipitation with alcohol is probably the oldest known method and has been used commercially. The big factor is the cost of alcohol, which must be carefully recovered or the venture is not profitable. Specially denatured alcohols—Formula 2 B containing 0.5 gallon of benzol per 100 gallons of ethyl alcohol, and 35*a* containing 5 gallons ethyl acetate per 100 gallons ethyl alcohol—have been approved for the commercial production of pectin. In using alcoholic precipitation it is found necessary to maintain the concentration of alcohol in the mixture at 50 per cent or more. The work of Poore[22] is a noteworthy contribution to our knowledge of the factors entering into the recovery of pectin from citrus fruit waste, and especially of the possible economic use of alcohol as a precipitant.

Pectin has been precipitated by the salting-out method,[10,20] but it is very difficult to remove the salt which is adsorbed by the pectin precipitate.

Attempts have been made to precipitate pectin by electrolysis,[3] but successful results have not yet been reported.

The method developed by the author and his co-workers[19] is based on the colloidal nature of pectin and involves the precipitation of a negatively charged particle by the introduction of a positively charged particle.

Process of Manufacture

Lemon refuse from citric acid manufacture contains about 2.5 to 4.0 per cent of pectin. Pectin in this case means alcohol precipitate minus ash determined on the total extract of the lemon pulp. The extraction is made with water containing 0.5 per cent sulfurous acid and consists of ten successive extractions of 1 hour each on a steam bath in beakers covered with watch glasses. The figure is arbitrary and based on an empirical method which gives comparative results.

The lemon refuse is cut or ground and heated to 95° to 98° C. for about 10 minutes to destroy pectinase, which converts pectin to pectic acid, thereby destroying its usefulness for jelly-making purposes. The pulp is then washed in cold water on a revolving screen to remove fine particles and the milky liquids, probably albuminoid suspensions, which if not removed cause cloudiness in the jelly in which the pectin is used.

This preliminary heating step may be eliminated and in practice is dispensed with when the peel is heated promptly for extraction, since that operation properly conducted destroys the pectinase.

EXTRACTION—The ground, washed peel is run into wood tanks having false bottoms covered with filter cloth; 500 to 1000 kg. is the usual charge of pulp. A 1 per cent sulfurous acid solution is added in sufficient quantity to suspend the pulp and the mixture is brought as rapidly as possible to about 90° C. The mixture is held at this temperature for 2 hours and is drawn off through the false bottom, the pulp itself making the filter mat. A second or third extraction is made in the same manner. Lemon pulp that has been cooked is a very soft mass and must be handled with extreme care or one has a tank full of mush from which it is almost impossible to get a clear pectin liquor. Probably the mechanical handling of the cooked pulp is the greatest single problem in the recovery of pectin from lemons.

The combined extracts or any one of them are filtered through paper pulp if necessary, and the pectin solution, which usually contains about 0.50 per cent pectin, is rapidly cooled and excess sulfur dioxide removed by passing it over a series of wooden baffle plates as in an ordinary water-cooling tower.

The solution is run into tanks of about 7500 liters capacity, the usual charge of liquor being 5000 liters.

Precipitation of Pectin—A sample is tested in the laboratory and the amount of reagents required for precipitation of the pectin determined. The theory of the precipitation is this:

> Pectin is a colloid of the emulsoid or lyophyllic type carrying a negative charge.
>
> Ammonia and aluminium sulfate produce aluminium hydroxide, which carries a positive charge, and a mutual precipitation of aluminium hydroxide and pectin occurs.
>
> The precipitation is ascribed by some to an actual chemical combination of the aluminium hydroxide and pectin, but the writer believes the mutual colloidal precipitation theory to be correct.

The reagents are carefully weighed and the aluminium sulfate is used in the form of a 25 per cent solution. While the pectin solution is in violent agitation the ammonia charge is dumped in practically instantaneously and is immediately followed by the aluminium sulfate, which is also added as rapidly as possible.

Best results are obtained when the quantities of ammonia and aluminium sulfate are such that after the mixture is complete the solution in which the precipitate is suspended has a minimum viscosity, which is usually at pH 4.0 to 4.2 determined colorimetrically using bromophenol blue as indicator.

Separation of Precipitated Pectin—The tank in which the precipitation is carried out is provided with a powerful wooden agitator and at several points around the sides of the tank there are heavy wood baffles. This construction makes it possible to agitate the mixture violently during precipitation and this whips air into the precipitate causing it to rise to the top immediately in a thick spongy mass. The mother liquor is withdrawn through a screen and excess aluminium sulfate is washed from the precipitate by a short agitation in cold water. It is finally drawn off through a screen and the excess solution removed by means of a basket centrifugal or a hydraulic press.

The pressed pectin precipitate is dried in a hot-air drier at about 65° C. The shorter the drying period the better the quality of the pectin. The dried pectin is a dark green, horny mass, which is ground in a mill of the swing hammer type and put through a 100-mesh screen.

The preparation at this stage may be used for making low-grade jellies, but it usually contains about 10 to 12 per cent of ash which is mostly aluminium hydroxide and contains some calcium and other mineral salts that carry through from the original extract. By very careful preparation of the extract with some sacrifice in yield it is possible to produce green pectin of good grade with but 6 or 7 per cent of ash.

Aluminium hydroxide is insoluble in alcohol, whereas aluminium chloride is soluble. The aluminium hydroxide existing as an impurity in the dry crude pectin is converted into aluminium chloride by suspending the ground dry pectin in 85 per cent alcohol containing about 10 per cent by volume of concentrated hydrochloric acid. The exact quantity of hydrochloric is calculated from a determination of the percentage of ash in the pectin to be washed. An excess of hydrochloric acid must be used, and this is removed by washing with neutral alcohol in which both hydrochloric acid and aluminium chloride are soluble.

The alcohol is drawn off through a cloth filter and recovered by distillation. The washed pectin is dried at a moderate temperature in a vacuum oven from which the alcohol is recovered and is then put through a screen for uniform sizing and packed for market.

The product resulting from this treatment is a grayish powder, which in jelly is neutral in color and flavor. It will carry from 140 to 220 times its own weight of sugar, depending on the condition of the fruit and the details of the various process steps. A standardized product is readily obtained by blending.

Present Commercial Products

Three types of pectin preparations are now on the market. Liquid concentrated pectin has become fairly familiar, as it is much used by the housewife as well as the jelly- and jam-maker. It contains usually about 4 to 4.5 per cent of pectin.

There are dry mixtures of pectin and sugar, put up both for the housewife and the jelly-maker, containing varying amounts of pectin. There is no uniformity as yet in the jelly strength of these mixtures, but a powder that will jell about forty times its weight of sugar is a very practical one.

Pure pectin is marketed in large quantities to jelly- and jam-makers or to producers of the pectin-sugar mixtures, and eventually will be available for use by the housewife in its purest and most economical and practical form.

Acknowledgment

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Bibliography

1—Beylik, U. S. Patent 1,393,660 (October 11, 1921).
2—Braconnot, *Ann. chim. phys.*, [II] **28**, 173 (1825).
3—Brown, *Am. Vinegar Ind.*, **2**, 14 (1923).
4—Caldwell, *Wash. Expt. Sta., Bull.* **147** (1917).
5—Chernoff, *Am. Food J.*, **18**, 200 (1923).
6—Crawford, U. S. Patent 1,507,338 (September 2, 1924).
7—Cruess and McNair, *J. Ind. Eng. Chem.*, **8**, 417 (1916).
8—Cruess and Lal Singh, *Calif. Agr. Expt. Sta., Circ.* **243** (1922).
9—Denton, Johnstin, and Yeatman, *U. S. Dept. Agr., Circ.* **254** (1923).
10—Doell and Maes, U. S. Patent 1,385,525 (July 16, 1921).
11—Dore, *Ind. Eng. Chem.*, **16**, 1042 (1924).
12—Douglas, U. S. Patent 1,235,666 (August 7, 1917).
13—Douglas, U. S. Patent 1,082,682 (December 30, 1913).
14—Ehrlich, *Chem. Ztg.*, **41**, 197 (1917).
15—Fellenberg, *Biochem. Z.*, **85**, Nos. 1–2, 118 (1918).
16—Goldthwaite, *Univ. Ill. Bull.* **11**, No. 31, 5th ed. (1917).
17—Hardy, *Biochem. J.*, **18**, 283 (1924).
18—Huber, U. S. Patent 1,410,920 (March 28, 1922).
19—Jameson, Taylor, and Wilson, U. S. Patent 1,497,884 (June 17, 1924).
20—Magoon and Caldwell, *Science* N. S. **47**, 592 (1918)
21—McKee, U. S. Patent 1,380,572 (June 7, 1921).
22—Poore, *U. S. Dept. Agr. Bull.* **1323** (1925)
23—Sucharipa, *J. Am. Chem. Soc.*, **46**, 145 (1924).
24—Sucharipa, *J. Assoc. Official Agr. Chem.*, **7**, 57 (1923).
25—Tarr, *Del. Agr. Expt. Sta., Bull.* **134** (1823).
26—Tarr, *Ibid.*, **136** (1924).
27—Tschirsch, Dissertation, Berne, **1908**.
28—Tutin, *Biochem. J.*, **15**, 494 (1921).
29—Tutin, *Ibid.*, **17**, 83 (1923).
30—Tutin, *Ibid.*, **17**, 510 (1923).
31—Dore, personal communication.

Control of Consistency in Manufacture of Cup Grease[1]

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CUP grease, which is the most common type of lubricating grease, consists of a mineral lubricating oil thickened with a calcium soap, or occasionally with a sodium soap or a mixture of the two. The data in the present paper, however, apply to greases made from calcium soap exclusively. From the standpoint of the user the consistency is perhaps the most important property, since because of the consistency he is willing to pay a higher price than for lubricating oil. Moreover, even small differences in consistency are important, especially in industrial lubrication, because they affect the rate of feed of the grease to the machine, and hence the consumption of the lubricant. The user is not unreasonable, therefore, in insisting upon a high degree of uniformity of consistency throughout the container and in succeeding purchases. The manufacture of cup grease of uniform consistency is not easy, however, because the consistency depends upon a colloidal gel structure and this structure, in turn, is subject to great variation with changes in composition and in conditions of manufacture.

General Method of Manufacture

The fats commonly used in the manufacture of cup grease are tallow, horse oil, cottonseed oil, and fish oil, but other fats and mixtures can also be used, and even fatty acids, with proper modification of the conditions of saponification to avoid lumping. The relative proportions of solid and liquid fatty acids affect the properties of the finished grease, and the data given later concerning the effect of temperature on consistency apply particularly to greases made from tallow. Considerable variation is possible in the details of the manufacture of cup grease, depending upon the kind and acidity of the fat used, the design of the mechanical equipment, and the personal preferences of the grease-maker. A typical method of procedure for calcium cup grease is as follows:

> The fat, of which tallow may be taken as an example, is weighed or measured into a steam-jacketed kettle equipped with a mechanical agitator of the paddle type, and a portion of the mineral oil, equal to about half the volume of the fat, is added to prevent the formation of lumps of soap during the saponification. A slight excess of hydrated lime in the form of a thin paste is then added and the mixture cooked, with agitation, until saponification is complete, which usually requires several hours. At times the mixture may boil up rather high in the kettle, and in such cases a small amount of mineral oil may be added each time to cause the foaming to subside. Completeness of saponification is judged by the texture of the soap, which, with the proportions of mineral oil mentioned above, should be firm and brittle when cold. A soft, pasty consistency indicates incomplete saponification or an excessive water content, whereas a stringy consistency indicates excessive evaporation of water, in which case additional water must be added. Mineral oil is then added slowly, to avoid chilling the grease with formation of lumps, until the consistency is reduced to the desired extent. The grease may then be drawn into packages, but preferably is first strained by pumping through some type of strainer to remove any lumps of soap or of hard grease.

For a No. 3 cup grease, which is the standard grade for use in compression grease cups for general lubrication, the final composition is usually about 18 per cent calcium soap, 1 to 3 per cent water, 1.8 per cent glycerol (if a fat, rather than fatty acid, was used) and the remainder, a mineral oil with a viscosity of about 100 to 150 seconds Saybolt at 100° F. (37.8° C.). The glycerol apparently has little effect upon the properties of the grease beyond influencing the general appearance and transparency, but the water is a very important ingredient. The chief disadvantage of excessive amounts of water is the undesirable color and opacity produced, but with insufficient amounts of water the consistency of the grease is affected. If the water content is somewhat below 1 per cent, for a grease of medium grade like No. 3, the gel structure is very pronounced but is easily broken down by mechanical working to give a mixture of comparatively low viscosity, and with still smaller amounts of water the gel may refuse to form and the grease have very little body. The probable reason for these phenomena is that in the presence of water the calcium soap is more or less hydrated and insoluble in the mineral oil, but in the unhydrated form tends to go into true solution in the mineral oil, or at least to form a colloidal solution rather than a gel. Under certain conditions—as, for example, through addition of water in the course of the reduction, with insufficient cooking to cause it to be taken up by the soap—it is possible to have the phenomena usually accompanying excessively low water contents, even though the water content as determined by analysis may be normal. This, of course, is due to an excessive proportion of water being present in the free condition merely as an emulsion in the grease rather than in combination with the soap.

Methods for Determination of Consistency

Except for the determination of consistency by feeling the grease in the container with the finger, probably the most common method has been to use some form of penetrometer, generally an asphalt penetrometer, such as the Dow or New York Testing Laboratory instrument, with special conical or cylindrical plungers or "needles" to adapt the machine to the testing of grease. Another instrument, designed originally for the testing of asphalt, which can be used for testing grease,[2] is the Abraham consistometer.[3] The present work has been done principally with this instrument, and a brief description of it will therefore be given.

The Consistometer

The Abraham consistometer is an instrument by means of which a plunger with a flat circular head and shank of reduced cross section can be forced into the sample at a uniform velocity. The force required to cause penetration is applied by means of a hand wheel and screw and is transmitted to the plunger through a spiral spring. The elongation of this spring is indicated by a pointer on a scale and gives the force directly in grams or kilograms. The rate of penetration is indicated by a hand which makes one revolution for 1 cm. of travel, and hence, to cause the plunger to penetrate at the standard rate of 1 cm. per minute, the force is applied at such a rate that the hand turns at the same speed as the second hand of a watch. Plungers are provided having

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[1] Received July 23, 1925. Presented before the Division of Petroleum Chemistry at the 70th Meeting of the American Chemical Society, Los Angeles, Calif., August 3 to 8, 1925.

[2] As suggested in Battle, "Industrial Oil Engineering," **1920**, p. 218.

[3] Abraham, "Asphalts and Allied Substances," **1918**, p. 498.

areas of 0.01, 0.1, 1, and 10 sq. cm., and also two springs, in order to adapt the instrument to the testing of substances throughout a wide range of consistency. The pressure applied to the sample is calculated by dividing the force in grams by the area of the head of the plunger in square centimeters, and for convenience, to avoid excessively large numbers, the cube roots of the pressures are taken as the Abraham hardness numbers or the Abraham consistencies.

The Abraham consistometer, rather than a penetrometer, was used in this work, primarily because of its adaptability to the testing of grease in comparatively small containers. It may be of interest, however, to discuss briefly the relative advantages and disadvantages of the two methods. Among the advantages of the consistometer is its adaptability to the testing of grease of all the usual grades from transmission grease to railroad greases, with results expressed on a single scale of numbers of convenient size and with larger numbers representing harder greases. With the consistometer it is also possible to note and allow for the presence of soft spots, cracks, and air pockets in the grease. Among the disadvantages of the consistometer are the somewhat higher cost of the instrument, the greater skill required in its operation, and the inapplicability, as at present designed, to the testing of grease in large containers. A disadvantage of the penetrometer at present is the lack of an established standard for the needle or cone, but this will probably be remedied in due course.[4] Cup grease, particularly in the unworked condition—that is, with the structure not disturbed by mechanical working—is a plastic solid, and hence the readings, both of the consistometer and of the penetrometer, depend upon both the yield point and the mobility. In a worked grease the effect of yield point is, of course, reduced, but it is found that a curve expressing the relationship between Abraham consistencies and penetrations with a 45-degree cone, for unworked grease, also holds fairly satisfactorily for worked greases.

Standard Consistencies for Cup Grease

To permit those not familiar with the consistometer to follow the subsequent data given in terms of Abraham consistencies, the consistencies and soap contents considered approximately normal for the usual commercial grades of calcium cup grease are given in Table I. These consistencies are determined at 77° F. (25° C.), since this is a convenient temperature and is standard for penetration of asphalt. For accurate work, it is desirable that the sample be brought to within about 1° F. of the standard temperature. Some work on the effect of the temperature of testing has shown that, for No. 3 to No. 6 cup grease, the normal temperature coefficient of change in consistency in the vicinity of 77° F. is around 0.02 to 0.03 point hardness, respectively, on the Abraham scale per degree Fahrenheit (0.036 to 0.054 per degree Centigrade), with the hardness decreasing, of course, as the temperature rises. These figures apply particularly to normal samples of calcium soap cup grease made from tallow, and some variation may be expected in batches having abnormal consistencies for the soap content.

Table I—Approximate Normal Consistencies and Soap Contents for Commercial Grades of Calcium Cup Grease

Grade	Approx. normal consistency (unworked) at 77° F.	Approx. normal soap content Per cent by wt.
0	2.0	10.5
1	3.3	11.5
2	4.5	14.5
3	6.5	17.5
4	8.5	20
5	11.0	22.5
6	16.5	29

In current work[5] on standardization of methods for determining the consistency of cup grease, consideration is being given to the advisability of using the consistency of the worked grease as a standard, rather than of the unworked grease. The worked consistency is determined upon a sample which has been worked mechanically, with care to avoid inclusion of air, until the consistency is substantially constant. The use of worked consistency has the great advantage, from the standpoint of inspection of purchases, that it permits testing of samples which have been transferred from one container to another. Also, the worked consistency may give an indication of the way in which the grease may function in a bearing or gear case, and the rate at which it will leak out. With the harder grades, however, and especially in use in compression grease cups or open boxes, the working in transferring the grease from the container to the cup or box is not sufficient to break down the structure completely to the worked consistency, and hence the unworked consistency will have some effect on the rate of feed of the grease to the bearing. From the standpoint of the manufacturer, the unworked consistency is of primary importance because of the prevalence of the custom of testing the consistency with the finger, and the certainty, under present conditions, that a grease which had an abnormally low unworked consistency, because of being drawn from the kettle at too low a temperature, would be considered too soft by the average customer, even though the worked consistency were normal. With standardized procedure and proper control of manufacture so that the product is uniform in quality, there need be no fear that the worked consistency of individual batches will be excessively low.

On typical samples of No. 5 to No. 2 calcium cup grease made entirely, or predominantly, from tallow, the ratio of the worked to the unworked consistency varied from about 50 to 70 per cent, with the greater drop in consistency usually taking place in the case of the harder greases. This is equivalent roughly to a drop of one or two commercial grades—that is, from a No. 5 to a No. 3 or a No. 3 to a soft No. 2. In appearance, however, a worked No. 5 cup grease is quite different from an unworked No. 3, since it is usually rather dull and pasty, even though care has been taken to avoid inclusion of air.

Quick Consistency Test for Grease in the Kettle

The chief difficulty in the control of consistency in the manufacture of cup grease lies in the fact that considerable time is required for the grease to attain its final set, and hence its final consistency, when a sample of the melted grease is drawn from the kettle and allowed to cool in the air. When drawn into 1-pound (0.5-kg.) cans, the final consistency is attained in about 3 days, whereas in wooden barrels about 5 days are required because of the slow cooling, particularly in the centers. A fairly close approximation to the final consistency can be obtained, however, by drawing a sample in a 1-pound can and allowing it to stand overnight before testing. This method of control is frequently used, but is not very convenient, particularly if the batch requires further reduction with oil. An attempt was made, therefore, to develop a more rapid method of testing, based upon the principle that by means of a low temperature of testing it is possible to compensate more or less perfectly for the incomplete setting in the limited time of cooling.

In preliminary work, the samples were taken in 1-pound slip-top cans 4 inches in diameter by $2^{1}/_{2}$ inches high (10.2 cm. by 6.3 cm.) and cooled in crushed ice and water. It was found that approximately 3 hours were required for the grease to reach a fairly uniform temperature of about 35° F.

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[4] The American Society for Testing Materials, Committee D-2, Subcommittee on Grease, is working on the standardization of a penetrometer cone for testing grease.

[5] A. S. T. M. Committee D-2, Subcommittee on Grease.

(17° C.), and that when the consistency was determined immediately after the cooling period the results gave a fairly satisfactory indication of the ultimate consistency of a sample cooled naturally. This period of cooling was considered excessive for a control test, however, and attempts were made to shorten it by the use of smaller cans. After rather unsatisfactory results with small cylindrical cans, because of formation of shrink holes and circular cracks, rectangular cans were tried with greater success.

The final procedure developed has now been in use for over two years, and has been a great improvement over previous methods. For taking the samples, spice cans of stock design are used. These are rectangular cans with slip tops and are $1^1/_4$ inches wide, $2^1/_4$ inches long, and $3^1/_8$ inches high (3.1 × 5.7 × 7.9 cm.). To reduce the trouble from cracks, the cans of grease are precooled in air for 15 minutes before being placed in the bath of crushed ice and water. They are left in the bath for one hour and then removed one at a time and tested immediately with the consistometer, two tests being made on each can. On the harder greases it is advisable to separate the grease from the sides of the can, after precooling, by running a spatula down next to the tin. This reduces trouble from cracks, but on No. 5 and No. 6 cup greases it is usually necessary to use special cans of the same size, but with removable bottoms, and to test the grease in an inverted position. It is also advisable to fill four to six cans each time, so that at least four consistency determinations can be made and averaged.

Application of Control Test for Consistency

In the manufacture of cup grease the consistency is dependent to such an extent upon the colloidal condition of the soap that the production of grease of standard consistency by making the batch according to a definite formula is very difficult, although a fair approximation can be obtained in a large proportion of the batches by careful standardization and control of all conditions of manufacture. Even with such careful control, however, a consistency test on the grease in the kettle before it is drawn into packages is very desirable in order to avoid the necessity of condemning or rebranding an occasional batch. In the application of the quick test just described, the grease in the kettle is first reduced with oil to give approximately the normal yield for the particular grade and is brought to the correct temperature for drawing. During this reduction the grease-maker keeps a rough check on the consistency by feeling samples removed from the kettle from time to time and cooled in the air. These samples may be obtained either by dipping a wooden paddle into the grease several times to build up a coating, or by pouring a small amount into a can cover.

When the batch is reduced to a point slightly on the hard side of the desired grade, samples are taken in spice cans and two samples are also taken in 1-pound cans. These latter samples are tested at 77° F., after standing for at least 3 days, and give a basis for determining the correspondence between the two tests under the current conditions, and also serve to reveal any serious errors in procedure. After the results of the quick test are reported to the grease-maker, the consistency of the grease in the kettle is adjusted, if necessary, by further addition of oil, and a second test is made. When a satisfactory result is obtained, the grease is again brought to the correct temperature for drawing and drawn into packages. The drawing of a batch of about 12,000 pounds (5500 kg.), particularly into small cans, requires considerable time, and care must be taken to prevent further changes in consistency during this period. As a control on these operations, samples for quick tests and standard 3-day tests are taken when one-third and two-thirds of the batch have been drawn, but the drawing is not delayed pending receipt of the results.

Control of Consistency during Drawing

After the batch of grease has been brought to the correct consistency for the grade, subsequent operations must be carried on in such a way as to avoid further changes. This involves, in particular, careful control of temperature until the grease is in the containers in which it will cool and set, since the temperature from which the grease cools without being disturbed has an important bearing on its final consistency. In general, if the grease is drawn at too low a temperature, particularly when a pump is used in the discharge line, the structure will be broken down to some extent by mechanical working in the kettle and in passing through the pump and lines, and the consistency will be lower than if the same grease were drawn at the proper temperature. This effect on the consistency is more marked in the quick test than in the standard test, however, and under such conditions the final consistency is likely to be higher than anticipated from the results of the quick test. At excessively low temperatures the mechanical working may be sufficient to give the grease an undesirable dull appearance or poor luster. If, on the other hand, the grease is drawn at too high a temperature, the consistency will be increased, but a so-called "false body" will be obtained. In such cases the gel structure is particularly marked and the difference between the unworked and worked consistency is abnormally large. For a No. 3 calcium cup grease made from tallow, the increase in consistency is about 0.15 point hardness on the Abraham scale per degree Fahrenheit (0.27 per degree Centigrade), within a short range above the normal drawing temperature, which is considered to be about 195° F. (91° C.)

In drawing grease into large containers, such as barrels and half-barrels, temperatures much above the normal drawing temperature are particularly to be avoided, because of the tendency for formation of soft centers under such conditions. Apparently, in the slow cooling from the high temperatures, changes take place in the colloidal condition of the soap so that the usual gel structure is not properly formed. In consequence, the grease in the centers of the large packages, instead of having an abnormally high consistency, or "false body," has an abnormally low consistency for the soap content, more like that of a worked grease. Under extreme conditions this loss of consistency in the centers of large packages may be more than two commercial grades.

From the foregoing it is apparent that the establishment of correct drawing temperatures is very important in avoiding "false body" and soft centers in large packages on the one hand, and loss of consistency by mechanical working on the other. These temperatures will vary both with the grade of the grease and the character of the soap, since lower temperatures can be used with the softer grades and with greases made from fats containing large proportions of liquid fatty acids. In applying the correct drawing temperatures, when determined, it is important not only to have the grease in the kettle at the proper temperature throughout the drawing, but also to have the grease as it enters the containers at substantially the same temperature. This necessitates the avoidance of poorly lagged lines, high steam pressure in steam-jacketed lines, or generation of a large amount of frictional heat in the pump. Aëration, from leaks in the suction line or excessive agitation in the kettle, is also to be avoided. With proper attention to these points, differences between the consistency of the grease in the kettle, as shown by the 3-day test, and the final consistency of the grease in packages may be kept down to very moderate proportions.

Interpretation of Results of Quick Test

As previously mentioned, the correspondence between the 1-hour quick test and the 3-day standard test is influenced somewhat by the temperature of the grease in the kettle when the samples are taken. Another cause of poor correspondence between the tests is reduction of the grease in the kettle with oil, without allowing sufficient time for the oil to enter into the proper combination with the soap. Under such conditions the quick test may show a greater reduction in consistency, from the addition of oil, than will be subsequently found in the standard test or in tests on the grease in packages. With standardization of the drawing temperature and of the procedure of taking the samples and of making the quick test, the relationship between the consistency determined by the quick test and the standard test should be satisfactorily constant. For greases made exclusively from tallow, this relationship is sufficiently close to equality to permit the quick results to be taken as a direct indication of the final consistency, but for greases made from fats containing greater proportions of liquid fatty acids, the quick results are usually somewhat low, especially for the harder grades of grease. For such greases, therefore, the relationship between the two tests is best expressed by means of a curve, and this curve then used to find the true consistency corresponding with the apparent consistency given by the quick test. This curve can be developed easily from the results of quick tests and 3-day tests on samples taken from the kettle at the same time, either while bringing the grease to grade or during drawing.

Acknowledgment

Acknowledgment is due H. R. Linhoff and P. S. Clarke for assistance in developing the details of the quick test and applying it to large-scale operations.

Manufacture of Hydrochloric Acid from Chlorine[1]

By Wilhelm Hirschkind

Great Western Electro-Chemical Co., Pittsburg, Calif.

The conversion of chlorine into hydrochloric acid, a reversal of processes marking the accomplishments of a Weldon and Deacon several decades ago has not only become an economic necessity due to the world-wide over-production of electrolytic chlorine, but for some time an accomplished fact. The combination of hydrogen and chlorine is carried out today in large installations at several plants, and has been described in detail by H. K. Moore and others. This phase of hydrochloric acid production will not be considered here.

The other reaction capable of converting chlorine into hydrochloric acid is the reversal of the Deacon process.

$$Cl_2 + H_2O = 2\ HCl + {}^1/_2\ O_2$$

A study of the equilibrium of this reaction shows that at lower temperature chlorine and at higher temperature hydrochloric acid is favored. The old Deacon process was therefore carried out at as low a temperature as the rate of reaction aided by a catalyst in form of cupric chloride would permit—between 480° and 500° C.

The Deacon chlorine process was one of the earlier examples of accurate equilibrium measurements carried out principally by Lunge and Marmier,[2] von Falkenstein,[3] and Lewis.[4] Von Falkenstein studied the reaction from both sides using a continuous flow method, whereas Lewis used a static method. With copper chloride as catalyst the lowest temperature at which equilibrium can be reached is 430° C. Above 500° C. copper chloride melts and naturally becomes impossible. Between 600° and 700° C. platinum chloride becomes a good catalyst, and between 900° and 1000° C. no catalyst is necessary.

At 577° C. the equilibrium constant of the Deacon process is one. Since the reaction is one of hydrogen with oxygen on one side and with chlorine on the other, this means that at this temperature the affinity of hydrogen to chlorine equals its affinity to oxygen. At higher temperature the affinity to chlorine, at low temperature to oxygen, predominates. Therefore, for production of hydrochloric acid by the reversed Deacon process only high temperatures are in question. The process has no technical interest, however, because the temperature at which the equilibrium is completely on the hydrochloric acid side becomes very high.

The reaction between chlorine and water—i. e., the reversed Deacon reaction assumes a new aspect if a reducing agent such as carbon is used to combine with the oxygen liberated by the reaction.

History of Method

Lorens[5] as early as 1895 clearly foresaw the trend of the chlorine and hydrochloric acid industries toward a manufacture of hydrochloric acid from chlorine. His paper contains scant experimental material, but he concludes that the reaction between chlorine, steam, and carbon at dull red heat proceeds according to the following equation:

$$C + Cl_2 + H_2O = 2\ HCl + CO \qquad (1)$$

Two years later Nauman and Mudford[6] published a comprehensive experimental investigation of the reaction between chlorine, steam, and carbon. Chlorine and steam were passed through a tube filled with carbon and heated to a definite temperature measured by a thermocouple which was inserted into the tube. The influence of variations in temperature, length of the layer of carbon, and excess water vapor was determined and the following conclusions were reached:

(1) The reaction within the temperature interval of 400° to 850° C. proceeds according to the equation

$$C + 2\ Cl_2 + 2H_2O = 4\ HCl + CO_2 \qquad (2)$$

contrary to the assertion of Lorens.

(2) The presence of carbon monoxide in the exit gas is due to a secondary reaction of the carbon dioxide on carbon.

(3) Excess water vapor results in the presence of water gas—i. e., a mixture of hydrogen and carbon monoxide in the exit gas.

If a rational discussion of this comprehensive experimental material had been attempted by the authors, it would probably have had some effect on the subsequent developments of the process. However, the later patents hardly took notice of this investigation.

Nagel[7] in 1912 described a practical gas generator in which

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[1] Received July 24, 1925. Presented as a part of the symposium, Chemical Industries of the West, before the Joint Meeting of the Divisions of Industrial and Engineering Chemistry, Paint and Varnish Chemistry, and Cellulose Chemistry at the 70th Meeting of the American Chemical Society, Los Angeles, Calif., August 3 to 8, 1925.

[2] *Z. angew. Chem.*, 105 (1897).

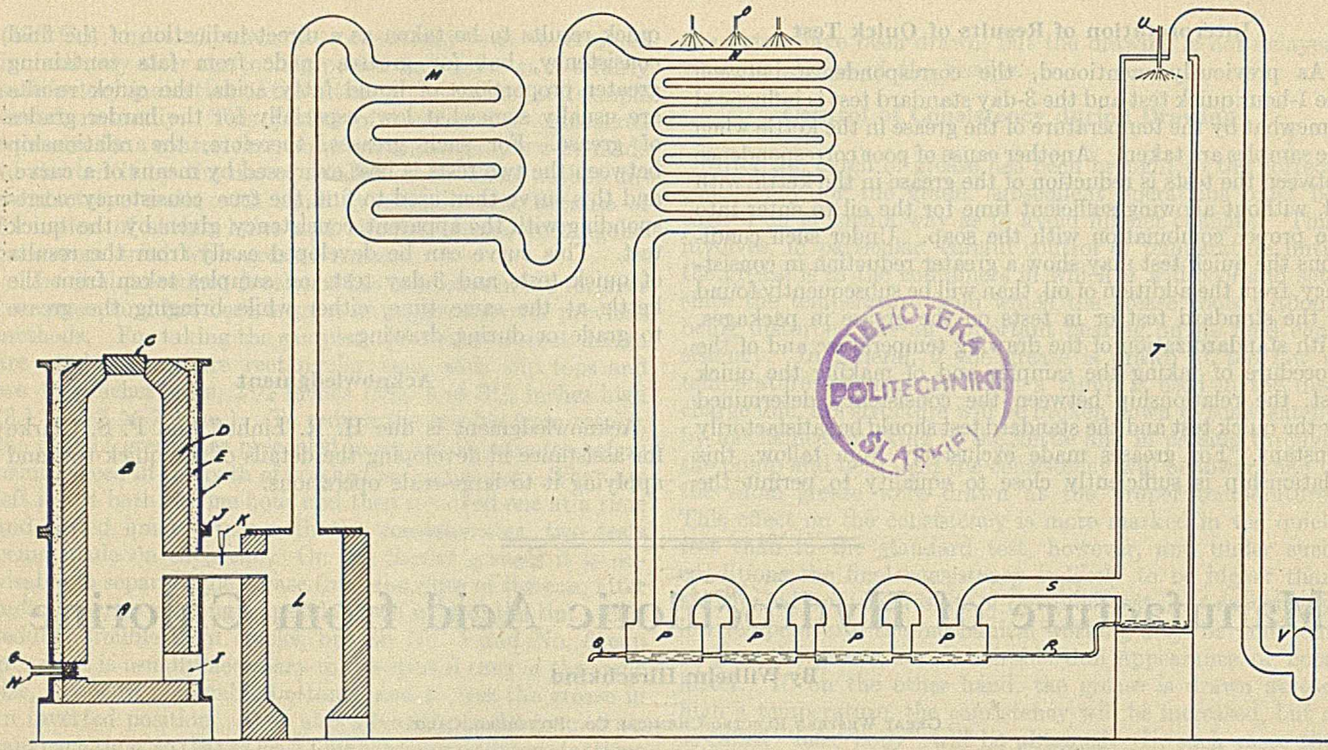
[3] *Z. physik. Chem.*, **59**, 313 (1907).

[4] *J. Am. Chem. Soc.*, **28**, 1380 (1906).

[5] *Z. anorg. Chem.*, **10**, 74 (1895).

[6] *Ber.*, **30**, 347 (1897).

[7] *Chem. Ztg.*, **36**, 54 (1912).



A—Reaction chamber
B—Coke storage
C—Furnace cover
D—Heat and acid resisting brick
E—Insulating material
F—Furnace shell
G—Chlorine inlet
H—Steam inlet
I—Cleanout
J—Joint
K—Pyrometer
L—Dust chamber
M—Air-cooled pipes
N—Water-cooled pipes
O—Spray nozzles
P—Tourills
Q—Acid outlet
R—Acid line
S—Gas line
T—Absorption tower
U—Spray nozzle
V—Fan

coke was heated to red heat by blowing with air and after turning off the air a mixture of chlorine and steam was passed over the red hot coke. He asserted that the reaction proceeded according to Equation 1, and might be run continuously by charging the coke in regular intervals through an upper door.

Peters[8] claims a process for quantitative conversion of chlorine into hydrochloric acid by means of coke and steam, at temperatures between the boiling point of water and red heat. Claims are also made for varying the mixtures of steam and chlorine without discussion, however, of the mechanism of the reaction, or the heat balance.

Gibbs[9] shows that the reaction between carbon, chlorine, and steam may be carried out between 0° and 130° C., producing hydrochloric acid and carbon dioxide. The important factors influencing the rate of the reaction are character of the charcoal, temperature, and ratio of chlorine to steam. Since only the best grades of absorptive charcoal can be used, the process, although interesting, is of no practical importance.

A U. S. patent granted to Paulus,[10] claims the simultaneous production of hydrochloric acid and carbon monoxide by the reaction between chlorine, carbon, and steam according to Equation 1. A certain amount of air, together with chlorine and steam, is admitted into the reaction chamber to supply the necessary heat by the combustion of carbon.

Two other patents cover the reaction between carbon, steam, and chlorine as carried out with an excess of water or steam for the purpose of taking up the heat of the reaction and at the same time absorbing the hydrochloric acid gas formed. Poma and Andreani[11] claim that the reaction proceeded somewhere between those represented by Equations 1 and 2, and that water in liquid form will serve as a medium to take up the heat of the reaction, and also as a condensing medium for direct production of liquid hydrochloric acid.

A very similar claim is made in a U. S. patent granted to Rosenstein.[12] The reaction is said to proceed according to Equation 2 and tables are given showing the excess steam required to keep the reaction temperature at a certain point. It is not mentioned, however, that the excess steam might react with the carbon, forming water gas, which would naturally escape with the exit gas.

Theory

The reaction according to Equation 1 liberates 7500 calories per mol hydrochloric acid formed, while the reaction according to Equation 2 will liberate 17,000 calories per mol hydrochloric acid.

It will aid in clarifying the situation if we consider the reaction as one between water gas and chlorine. The water gas reaction, because of its outstanding technical interest, has been studied from many angles. It is well known that at 600° C. the reaction is mainly:

$$C + 2\,H_2O = CO_2 + 2\,H_2 \qquad (3)$$

while at 1000° C. it very nearly approaches:

$$C + H_2O = CO + H_2 \qquad (4)$$

The interval between these temperatures is represented by gas compositions given in Table I.

Table I—Percentage Composition of Resulting Gas

Temperature of carbon ° C.	H_2	CO_2	CO
600	66	30	4
700	65	29	6
800	62	23	15
900	54	7	39
1000	50	2	48

Let us now consider the hydrochloric acid formation in connection with the water gas reaction according to Equations 3 and 4.

$$\begin{array}{ll} C + 2\,H_2O = CO_2 + 2\,H_2 & (3) \\ 2H_2 + 2\,Cl_2 = 4\,HCl & \\ \hline \text{or} \quad C + 2\,H_2O + 2\,Cl_2 = 4\,HCl + CO_2 & (2) \end{array}$$

and

$$\begin{array}{ll} C + H_2O = CO + H_2 & (4) \\ H_2 + Cl_2 = 2\,HCl & \\ CO + Cl_2 = COCl_2 & \\ COCl_2 + H_2O = CO_2 + 2\,HCl & \\ \hline \text{or} \quad C + 2\,H_2O + 2\,Cl_2 = 4\,HCl + CO_2 & (2) \end{array}$$

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[8] U. S. Patent 1,229,509 (1917).

[9] This Journal, 12, 538 (1920).

[10] U. S. Patent 1,420,209 (1922).

[11] British Patent 189,723 (1923).

[12] U. S. Patent 1,485,816 (1924).

Evidently, the result is the same no matter at what stage of the water gas equilibrium the chlorination takes place. The same result could have been obtained by a thermodynamic calculation, and is proved by the experimental results of Nauman and Mudford, as well as those of the writer, which show that the carbon monoxide in the exit gas is formed secondarily by the action of carbon dioxide on the hot carbon and also that excess steam will result in water gas escaping with the hydrochloric acid and carbon dioxide. Both the reduction of carbon dioxide to carbon monoxide and the water gas reaction are endothermal, and if they would take place to a considerable extent the system would cool below reaction temperature, therefore necessitating heat from outside sources. In order to be independent of outside heat, the reaction must be controlled so that it will proceed only according to Equation 2. In this form the reaction is obviously the most economical one for hydrochloric acid formation from steam, chlorine, and carbon. It uses the minimum amount of carbon and produces the highest concentration of hydrochloric acid gas, without requiring outside heat. The absence of combustible constituents in the gases leaving the reaction zone makes this process also the safest.

Experimental

It was found by experimenting on a large scale that by regulating the height of the coke layer to the rate of admission of chlorine an exit gas practically free from chlorine and carbon monoxide could be obtained, running as high as 73 per cent hydrochloric acid. It could further be demonstrated that excess steam for the purpose of carrying off the heat of reaction is unnecessary, besides being for above-mentioned reasons undesirable. Working with theoretical proportions of steam and chlorine, the exit gases leave the furnace at a temperature of about 900° C., at which the apparatus can be easily maintained.

The theoretical exit gas based on a 90 per cent chlorine gas should contain 76.5 per cent hydrogen chloride and 19 per cent carbon dioxide. The analyses of the exit gas (Table II) show the results of two experiments with approximately 90 per cent chlorine gas and an amount of steam allowing for 2.5 per cent excess entering the reaction chamber. The rate of chlorine in Experiment 1 was 95 kg. per hour, in Experiment 2, 105 kg. per hour.

Table II—Analyses of Exit Gas

Constituent	Expt. 1 Per cent	Expt. 2 Per cent
HCl	73.5	72.0
Cl_2	..	0.18
CO_2	17.0	18.10
CO	3.0	..
O_2	0.25	0.47
N_2	6.25	9.25
	100.00	100.00

Ratio $\frac{CO_2 + \frac{1}{2} CO}{HCl} = 1:3.98$ Ratio $\frac{CO_2}{HCl} = 1:3.97$

These two experiments represent the best conditions. If a hydrochloric acid entirely free from chlorine is desired, conditions of Experiment 1 should be chosen, though there may be small amounts of carbon monoxide in the exit gas.

Apparatus

The apparatus used by the Great Western Electro-Chemical Company is simple. The furnace consists of a stack lined with high-temperature fire brick of acid-proof material with an inside diameter of 2 feet and a height of 8 feet. The lower part of the stack up to the gas outlet comprises the reaction chamber, while the upper part is used for storing and preheating the coke. Chlorine and steam enter through separate pipes at the bottom of the stack, and the coke is charged through the top at regular intervals. The height of the gas outlet should be chosen according to the rate of the gas flow, in order to provide a coke layer of proper size. Running with nearly theoretical proportions of steam and chlorine, the gases leave the reaction chamber at temperatures between 800° and 950° C. They first pass through a dust chamber made of the same material as the furnace lining, from there through an air-cooled, and then through a water-cooled system of silica pipes. The cooled gases finally enter a system of Tourills, with an absorption tower at the end made from tile pipe and filled with standard tile tower filling. A fan at the end of the absorption tower draws the gases from the furnace through the cooling and absorption system.

Operation

To start the reaction the coke is heated with an air blast to bright red heat. As soon as the proper temperature is reached the air is removed and chlorine and steam are admitted, whereupon the reaction begins at once and maintains itself. With 80 to 85 per cent chlorine gas an exit gas containing 65 to 70 per cent hydrochloric acid can be maintained. There is practically no condensation in the pipe system, and the cooled gases of above composition enter the Tourills, where the absorption to a 32 to 38 per cent hydrochloric acid takes place. The gases leaving the Tourills and still carrying a small amount of hydrochloric acid pass through the absorption tower before being discharged into the atmosphere.

The coke most suitable for the purpose is a high-grade oil or gas coke as free as possible from ash and tar.

Comparison with Water Gas Process

A comparison of this process with the technical water gas process is interesting. The technical water gas process consists in blowing hot carbon alternatingly with air and steam. It is a combination of the heat-liberating combustion of carbon with the heat-consuming water gas reaction. Both reactions cannot be carried out simultaneously, because the water gas would be diluted with air and carbon dioxide. In the hydrochloric acid process, the heat-consuming water gas reaction is combined with the heat-generating chlorination, whereby the constituents of water gas are converted into hydrochloric acid and carbon dioxide. For this reason the two reactions can be carried out simultaneously.

It has been proposed that the process be conducted in two steps, by first generating water gas, which is then chlorinated in a second apparatus according to the reaction:

$$2 Cl_2 + H_2O + CO + H_2 = 4 HCl + CO_2$$

It is obvious from the foregoing, however, that in doing so one would loose, besides simplicity of operation, the important advantage of this process which is the utilization of the heat of hydrochloric acid formation to maintain the water gas reaction.

Calendar of Meetings

American Water Works Association (Central States Section)—Annual Meeting, Erie, Pa., October 9 and 10, 1925.

Institute of American Meat Packers—Annual Meeting, Chicago, Ill., October 16 to 21, 1925.

American Welding Society—Fall Meeting, Massachusetts Institute of Technology, Cambridge, Mass., October 21 to 23, 1925.

Association of Official Agricultural Chemists—41st Annual Meeting, Raleigh Hotel, Washington, D. C., October 26 to 28, 1925.

American Institute of Chemical Engineers—Cincinnati, Ohio, December 2 to 5, 1925.

American Chemical Society—71st Meeting, Tulsa, Okla., April 5 to 9, 1926.

Association of Chemical Equipment Manufacturers—2nd Chemical Equipment Exposition, Cleveland, Ohio, May 10 to 15, 1926.

The Decomposition of Liquid Hydrocyanic Acid[1]

By Mark Walker and D. N. Eldred

The Pacific R. & H. Chemical Corp., El Monte, Calif.

During the past few years large quantities of liquid hydrocyanic acid containing 96 to 98 per cent HCN have been manufactured, transported over the public highways, and stored in warehouses, or specially constructed sheds, for indefinite periods of time. Numerous explosions have occurred in attempting to store the liquid confined in closed containers. Because of the high toxicity of the materials to nearly all forms of life, and the violence of the explosions, it became increasingly important to determine the causes of these explosions.

A study has been made of the behavior of liquid hydrocyanic acid, confined in steel bombs under controlled temperatures and pressures, alone and in the presence of catalysts and stabilizers. In this study, time-temperature and time-pressure curves and the character and composition of the products of the reaction have been determined.

The explosions were found to result from the rupturing of closed containers due to the formation of gases caused by the exothermic polymerization and decomposition of the liquid. Pressures of over 1000 pounds per square inch were frequently experienced. At atmospheric temperature, polymerization without a sudden rise of pressure may result from the balance established between the heat of reaction due to decomposition and the loss of heat by radiation.

The products of the reaction were (1) a solid black mass resembling willow charcoal or powdered carbon, which upon analysis proved to be a polymer of hydrocyanic acid slightly deficient in hydrogen and nitrogen, and (2) various gases among which ammonia and carbon monoxide predominate.

Gaseous mixtures of hydrocyanic acid and air varying from 11 per cent to 60 per cent of HCN by weight, will explode when ignited. It is believed, however, that the explosions mentioned in this work do not belong to this class.

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NEF[2] states that, although absolutely pure hydrocyanic acid is an extraordinarily stable substance, the aqueous solution rapidly decomposes but the presence of a trace of mineral acid renders this solution more stable.

Owing to occasional unexplained explosions dating back over a long period of years, liquid hydrocyanic acid has gradually acquired the reputation of being an unstable compound, while with its introduction into practical fumigation for various purposes these explosions have not only become more numerous but have been on a larger scale. It has been determined in this laboratory that gaseous mixtures of hydrocyanic acid and air may be made to explode when mixed in percentages by weight varying from 11 to 60 per cent of HCN. The explosions mentioned above were, however, not of that nature, but were produced entirely by exothermic reactions occurring in the liquid within a closed container. As examples of the various occurrences the following instances are cited:

In 1861 Professor Campani, of the University of Siena, described a violent explosion that took place in his own laboratory. In August, 1862, Professor Polacci[3] observed a similar explosion. On March 8, 1918, in the laboratory of Mark Walker, in Los Angeles, Calif., a pint bottle containing liquid hydrocyanic acid exploded with a report like that of a shot gun and threw fragments of glass and a cloud of black dust all over the room. On December 27, 1920, a 2.5-liter green glass bottle partially filled with liquid hydrocyanic acid exploded in the laboratory of The Pacific R. & H. Chemical Corporation, in Los Angeles, with a loud report, scattering glass and a black solid over a wide area. On May 22, 1918, at Perth Amboy, N. J., a drum containing liquid hydrocyanic acid blew up with a report that was heard over an area of several city blocks, the force of the explosion breaking about thirty-five window panes in a nearby building. In July, 1921, an explosion of a drum of liquid hydrocyanic acid in Alhambra, Calif., caused the death of two horses, a number of chickens and pigeons, and rendered unconscious five men, while a boy nearly lost his life.

As very large quantities of an aqueous solution containing 95 to 98 per cent of hydrocyanic acid are now being used in the fumigation of citrus trees for controlling scale insects, as considerable quantities of this liquid are also being used for the extermination of vermin in ships, warehouses, and other places as well as for the fumigation of various articles of food, and as all this material is being transported over public highways with attendant risk, an investigation into the stability of the liquid seemed necessary. The purpose of this study was also to determine the nature of the causes that led to explosions and to see whether these explosions were due to the spontaneous rupture of the hydrocyanic acid molecule with the formation of a larger volume of other gases or simply to excessive gas pressure within the container.

Previous qualitative experiments in this laboratory had shown that the introduction of hydroxyl ion into liquid hydrocyanic acid promptly started decomposition, which was primarily manifested by a yellow color in the liquid and subsequently by the deposition of a black solid, resembling powdered willow charcoal. It had been found at the same time that sulfuric acid added in moderate concentration, as well as certain other stabilizing agents, retarded this change.

These facts are in accord with the conclusions reached by various other investigators. Nef[2] states: "If the acid contains traces of impurity such as water or potassium cyanide it rapidly turns brown, forming the so-called azulmic compounds, about which very little is known. The aqueous solution rapidly decomposes, especially if exposed to the light, forming a brown precipitate of azulmic acid, while ammonia, formic and oxalic acids, and other substances remain in solution." Richter,[4] in addition to the above, mentions the formation of white crystals soluble in ether and having the same percentage composition as hydrocyanic acid, which break down on boiling into glycocoll, carbon dioxide, and ammonia, which decompose at 180° C. with explosion and partial reformation of hydrocyanic acid.

Prior to the investigations described herein, the writers had determined that when liquid hydrocyanic acid was heated in a sealed container the liquid changed completely into a

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[1] Received July 17, 1925. Presented as a part of the Symposium on Chemical Industries of the West at the Joint Meeting of the Division of Industrial and Engineering Chemistry, Section of Paint and Varnish Chemistry, and Division of Cellulose Chemistry at the 70th Meeting of the American Chemical Society, Los Angeles, Calif., August 3 to 8, 1925.

[2] *Ann.*, **287**, 377 (1895).

[3] Salomone, *Boll. chim.-farm.*, **6**, 237 (1862).

[4] 3rd American Edition, **1913**, Vol, I, p. 229.

solid black substance, and frequently this change was accompanied by a sudden rise of temperature and pressure.

On the basis of these facts, plans were made to study the behavior of liquid hydrocyanic acid alone, as well as in the presence of catalysts and of stabilizers, when subjected to heat and pressure in a sealed vessel, noting the elapsed time before active decomposition began, the rise of temperature and of pressure during the active period, as well as the character and composition of the products of the reaction.

Inasmuch as at ordinary atmospheric temperature it had been found that the length of the primary reaction period was uncertain, as well as frequently extremely long, it was decided to accelerate the reaction by means of externally applied heat, thus economizing in time.

Procedure

A fixed quantity (250 cc.) of pure liquid hydrocyanic acid was confined in a steel bomb and continuous, definite pressure, produced by heat from a gas flame applied to the exterior of the bomb, was maintained till a sudden rise of the pressure indicated that what may be termed the "secondary" reaction period had commenced. At this point the gas flame was immediately shut off, the elapsed time, in hours, was noted, and frequent readings of temperature and pressure were taken while the pressure rose to, and definitely receded from, a maximum.

Experiments with liquid hydrocyanic acid alone were made in which the initial pressure was maintained at 50, 75, 100, 150, and 200 pounds per square inch. These experiments were followed by others in which liquid hydrocyanic acid stabilized with certain reagents was used, throughout the same pressure range, and these in turn were followed by experiments in which the liquid hydrocyanic acid was catalyzed by suitable compounds.

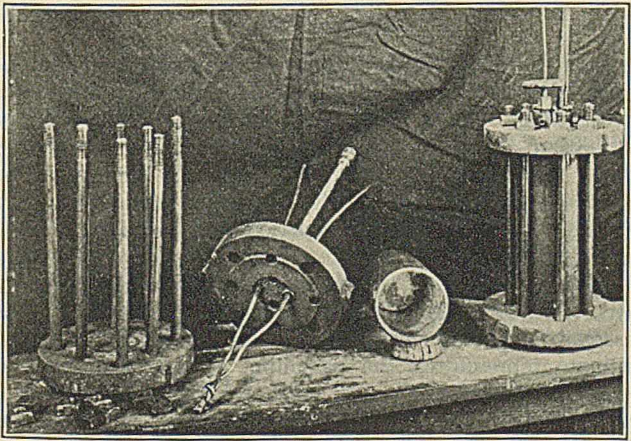


Plate I—Bomb Disassembled

In many cases after the reaction had ended, and the bomb had cooled to atmospheric temperature, the gases were withdrawn and analyzed. The solid material was then removed and stored for future analysis, while the bomb was cleaned, retinned if necessary, and put back into service.

Apparatus

In order to confine the liquid while under observation, bombs (Plate I) were constructed from sections of steel tubing 7.36 cm. inside diameter and 19.05 cm. long, with walls 0.30 cm. thick. These sections were closed by welding to one end a circular steel disk, thus making a cylindrical thimble having a capacity of 810 cc. The other end of the thimble was carefully smoothed off and was tapered slightly on the outer edge. When in use the thimble was held in a vertical position between two solid iron flanges, 25 mm. (1 inch) thick by 165 mm. ($6^1/_2$ inches) diameter, having seven equally spaced 15-mm. ($^5/_8$-inch) holes for the reception of 13-mm. ($^1/_2$-inch) bolts around their circumferences. In sealing the bomb, a soft copper ring was laid between the upper edge of the thimble and the lower side of the top plate, after which the nuts on the bolts were screwed down, thus making a gas-tight joint.

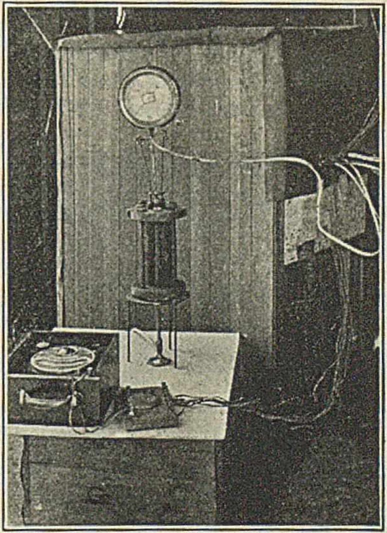


Plate II—Diagrammatic Assembly of Bomb Showing Temperature and Pressure Recorders

The iron cover had a centrally located hole threaded for a 6-mm. ($^1/_4$-inch) black iron pipe to connect with a pressure gage; two 6-mm. ($^1/_4$-inch) holes fitted with stuffing glands through which the thermocouple leads projected outward; and a fourth hole into which was screwed a needle valve, for sampling the gases. The inside of each bomb was carefully coated with metallic tin.

The internal pressure was shown by a standard 1000-pound steam gage, and the internal temperature was indicated on a pyrovolter (Plate II). The lower end of the naked thermocouple was directly immersed in the liquid in the bomb, and the two upper ends were taken out through separate stuffing boxes which were packed with asbestos wicking. From these extremities wires led to a cold junction, maintained at a constant temperature by being located in an insulated metal compartment which communicated by means of a metal wall with an ice box kept constantly full of ice. By this means the pyrovolter readings never deviated more than 3 degrees from the true temperature in the bomb. In order to detect a sudden rise of pressure, each gage was equipped with an electrical contact which could be so set that a bell would automatically ring continuously when any desired pressure was reached.

The bombs rested on angle iron supports and each bomb was individually heated by a suitably adjusted Bunsen burner located directly underneath. Six bombs were operated simultaneously. These were located in a strongly built bomb house 4 × 4 × 8 feet, adjacent to the laboratory, in which the pyrovolter was situated (Plate III).

A selective switch enabled the operator to take the temperature of any desired bomb. The pressure gages were mounted on the front of the bomb house in such a manner that they could be read from the laboratory by means of a telescope, which was constantly trained upon them.

Preparation of Liquid Hydrocyanic Acid

Commercial liquid hydrocyanic acid averaging from 96 to 98 per cent HCN, with from 2 to 4 per cent of water, after slight acidification with sulfuric acid was redistilled one or more times as necessary till it was of the desired purity. In order to minimize the contamination by impurities the distillate was condensed in a block tin coil and was received and stored in tin-lined receptacles so that at no time after distillation was it in contact with glass or any metal other than tin. The final product which was used for the experimental work contained at least 99.9 per cent HCN with 0.0010 per cent or less of sulfuric acid.

Methods of Analysis

Gases—The gases in the bombs were, in many cases, analyzed for hydrocyanic acid, ammonia, carbon dioxide, heavy hydrocarbons, oxygen, carbon monoxide, hydrogen, methane, and nitrogen. The last six of these were determined by ordinary gasometric methods of analysis using mercury as a confining medium. Hydrocyanic acid, ammonia, and carbon dioxide were determined separately. Four portions of 100 cc. each were successively withdrawn from the bomb.

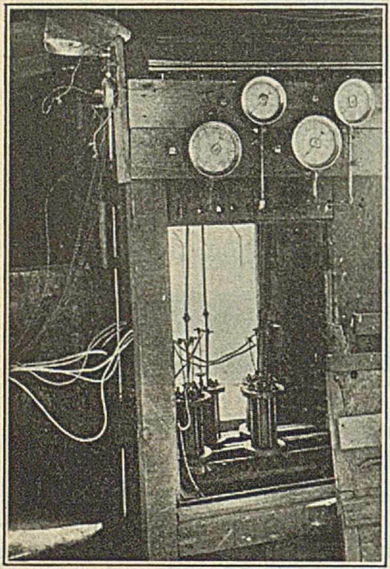


Plate III—Bombs in Position in Bomb House with Pressure Gages, Cold Junction Box, and Electric Alarm

The first portion was passed very carefully and gradually into a 25-cc. cylinder containing an excess of 0.2 *N* hydrochloric acid. The excess of hydrochloric acid was then titrated with 0.1 *N* sodium hydroxide, after which the ammonia volume was calculated.

The hydrocyanic acid was determined by passing a second portion of the gas into 25 cc. of 10 per cent sodium hydroxide solution, after which the liquid was titrated with standard silver nitrate solution using potassium iodide indicator.

The carbon dioxide was determined by passing a third portion of the gas into 25 cc. of 10 per cent sodium hydroxide solution, free from carbon dioxide, and precipitating the carbon dioxide with barium nitrate solution, then determining the carbon dioxide by ordinary titrometric methods.

The fourth portion of gas was passed into a Hempel pipet containing an aqueous solution of sulfuric acid (1:8), which removed both the ammonia and the hydrocyanic acid. As the latter volume was already known the difference gave the ammonia. From this point the regular gasometric procedure was followed.

Solid Products—The determination of moisture was made in an air bath at 110° C., after which the ash determination was made by carefully igniting the same portion. Standard methods for elementary organic analysis by combustion were used in determining the carbon, hydrogen, and nitrogen in the sample. All analyses were calculated to, and are reported in, the water- and ash-free condition.

Products of Reaction

The products of the decomposition of hydrocyanic acid held in a closed container were a solid black mass, resembling willow charcoal or powdered carbon, accompanied by various gases, mainly ammonia and carbon monoxide. In some cases transparent crystals were found upon the cold walls of the bomb. Upon exposure to the air these crystals became brown or black and on analysis proved to be ammonium cyanide. On account of this crystal formation the gases in the bomb were allowed to cool to atmospheric temperature before being analyzed, as if drawn out while hot the crystals would form on the walls of the gas buret, thus vitiating the results.

Catalysts and Stabilizers

For the purpose of this investigation a catalyst was regarded as a substance that would cause liquid hydrocyanic acid to become yellow and finally change into a solid product with or without the liberation of perceptible quantities of gas. In like manner a stabilizer was considered as a substance that would prevent hydrocyanic acid from undergoing the above-mentioned change. The following substances were classed as catalysts: ammonia, sodium hydroxide, sodium cyanide, and water; sulfuric acid and metallic copper were classed as stabilizers.

Table I shows the amount and kind of reagents added to the standard quantity of hydrocyanic acid in the different experiments. In general for each system separate experiments were run at 50, 75, 100, 150, and 200 pounds pressure during the preliminary or incubation period.

Table I

System	Reagents Added to 250 Cc. Liquid Hydrocyanic Acid	Per cent
1	None	
2	0.4250 gram gaseous ammonia	0.24
3	1.8250 grams gaseous ammonia	1.04
4	6.7500 grams gaseous ammonia	3.86
5	1.0000 gram powdered sodium hydroxide	0.57
6	1.1250 grams powdered sodium cyanide	0.64
7	17.5 cc. water	10
8	0.0070 gram concentrated sulfuric acid	0.004
9	0.00175 gram concentrated sulfuric acid	0.010
10	1 gram powdered sodium hydroxide, allowed to react for 2 hours, then sulfuric acid added till there was 0.0070 gram in excess present	0.004
11	Same procedure as System 10, but substituting 1 gram of sodium cyanide	
12	Same procedure as System 10, but substituting 1.775 grams of gaseous ammonia	
13	17.5 cc. of water, 10 per cent, and 0.0070 gram sulfuric acid	0.004
14	0.0070 gram sulfuric acid, 0.004 per cent, and 18 grams of copper screen	10
15	18 grams of 12-mesh copper screen	10

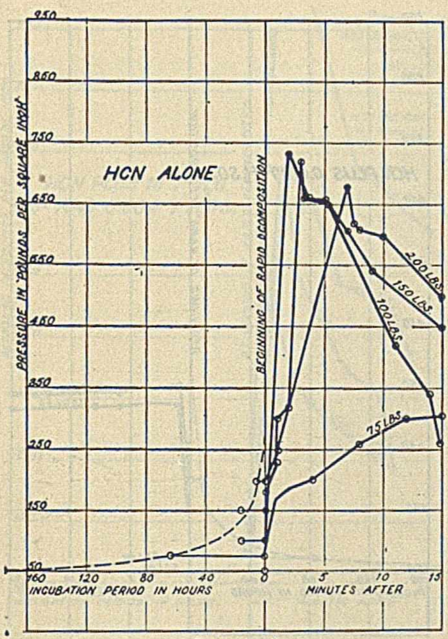
Data on Pressure

From the data obtained, sets of curves based on the observed pressures have been plotted for the fifteen systems investigated. These curves show the length of the primary incubation period, at constant pressure, in hours, and the length of the secondary reaction period in minutes. The extreme left-hand ends of the abscissas, representing the lengths of the primary reaction period, form points on a curve which probably shows the life of liquid hydrocyanic acid in hours when subjected to pressure generated in the bomb by heat. Although experimental evidence is lacking, it is reasonable to believe that the junction of this curve with the ordinate representing the beginning of the final reaction period shows the pressure at which anhydrous liquid hydrocyanic acid would promptly decompose if raised by the aid of heat to that point.

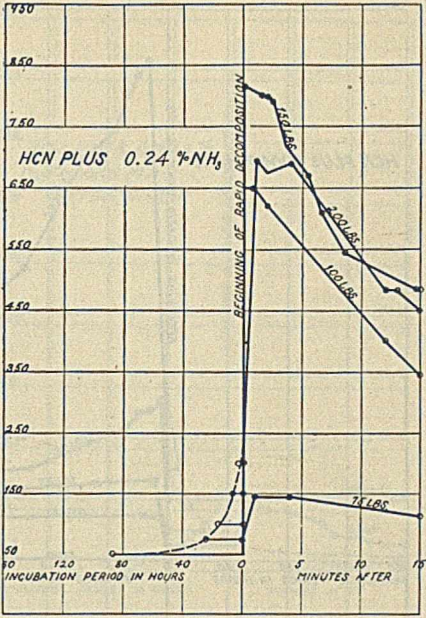
In several graphs the words "lbs. rise" are used on account of the height of the curves which rise beyond the limits of the graphs; in such cases the figure denotes total pressure.

From a consideration of the pressure curves for pure hydrocyanic acid alone it is seen that at 50 pounds pressure the reaction proceeded without any notable rise in pressure. In such cases the end point was obtained by trial as follows: At frequent intervals the lamp flame was suddenly raised for a brief period while the pressure gage was observed for rise in pressure. If there was liquid present in the bomb an immediate rise in pressure was noted, but if all the liquid had passed into the solid phase only a very small rise in pressure could be noted. Several tests were run so as to obtain the end point with accuracy.

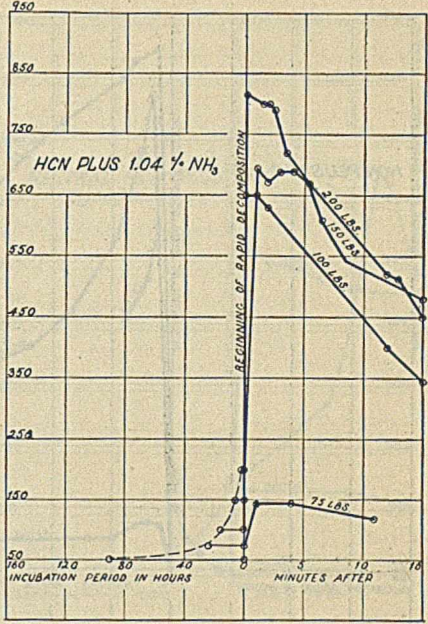
At 75 pounds the rise in pressure was well defined, while at 100, 150, and 200 pounds the rise was very sharp, re-



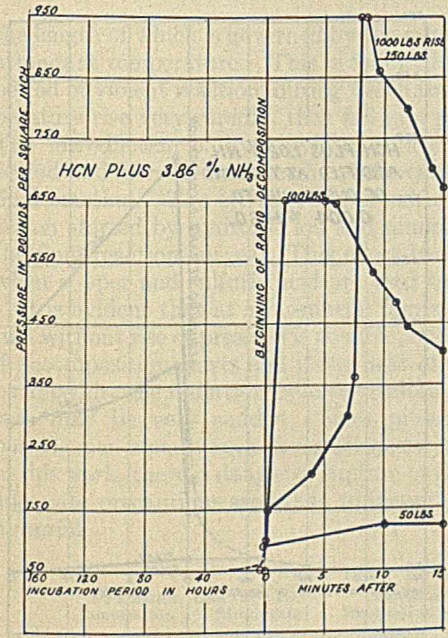
System 1



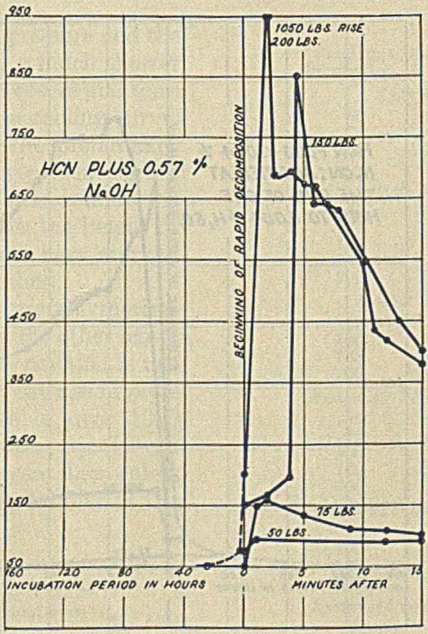
System 2



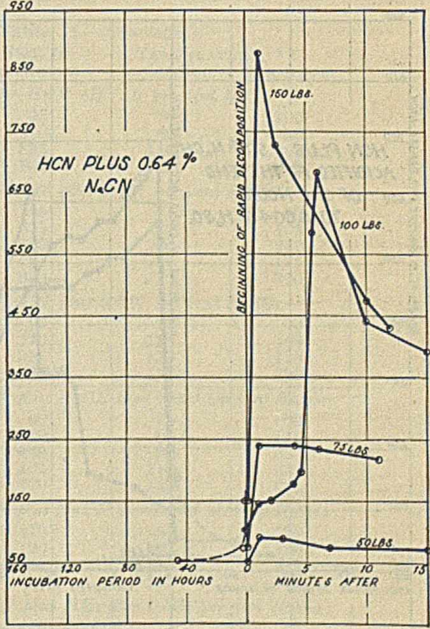
System 3



System 4



System 5



System 6

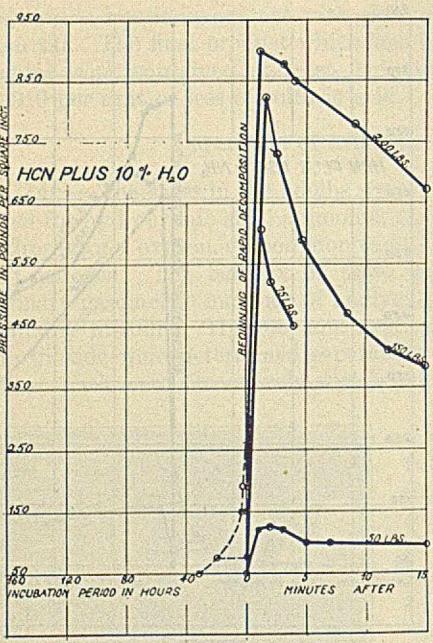
sembling an explosion. The derived curve (dotted line) denoting the length of the period of incubation rises very steeply after 75 pounds pressure is reached.

From this work there seems to be, at the lower pressures (and corresponding temperatures), a comparatively long period of relative inactivity which, at the lowest pressure used, may result in complete solidification of the liquid phase without elevation of the pressure, but in the case of the higher initial pressures invariably terminates with the sudden exothermic decomposition of some part of the constituents, thus producing the observed sharp rise in temperature and pressure.

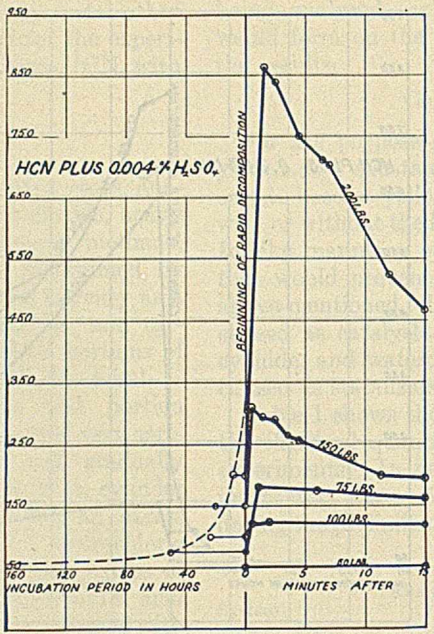
If the curves for the system hydrocyanic acid plus ammonia (0.24 per cent) are compared with those for hydrocyanic acid alone, it will be seen that in every instance in the presence of ammonia the incubation period has been reduced approximately one-half and the decomposition curves are in general a little steeper. On increasing the percentage of ammonia to 1.04 per cent the time of the incubation period becomes still shorter and the decomposition curves tend to rise higher. This rise, however, may be due partly to increased pressure in the system produced by the external addition of ammonia.

By using sodium hydroxide in percentage equivalent to 0.24 per cent of ammonia, the time of incubation is reduced about three-fourths and nearly every decomposition curve rises much higher than with the corresponding amount of ammonia. With sodium cyanide, corresponding in molecular equivalent to the aforementioned two compounds, the period of incubation and the rise of the decomposition curves fall between those for ammonia and sodium hydroxide.

When 10 per cent of water is used the incubation period becomes—as would be expected from the familiar reaction used to express the decomposition of hydrocyanic acid ($HCN + 2H_2O = HCOOH + NH_3$)—very much shorter, being only about one-fifth of the time required for pure hydrocyanic acid and about one-half of that required for 0.24 per cent ammonia. These curves with water are in general



System 7



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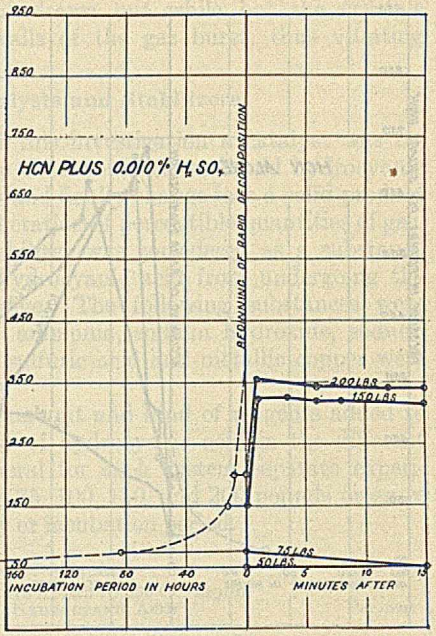
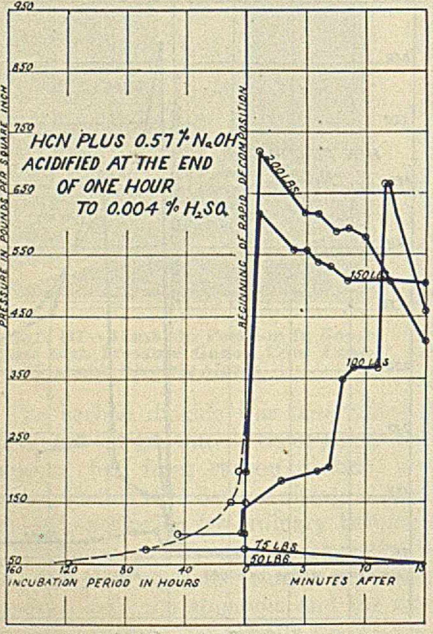
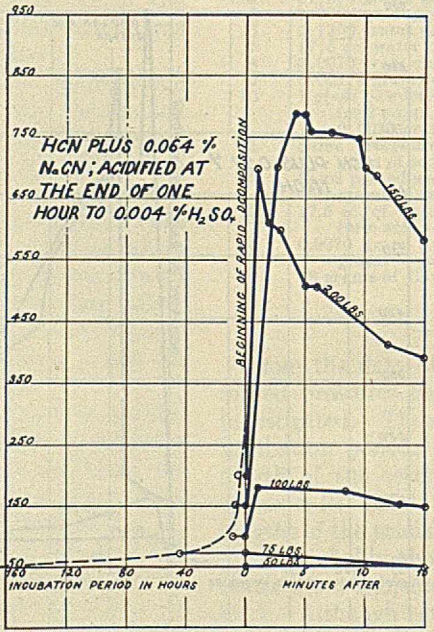


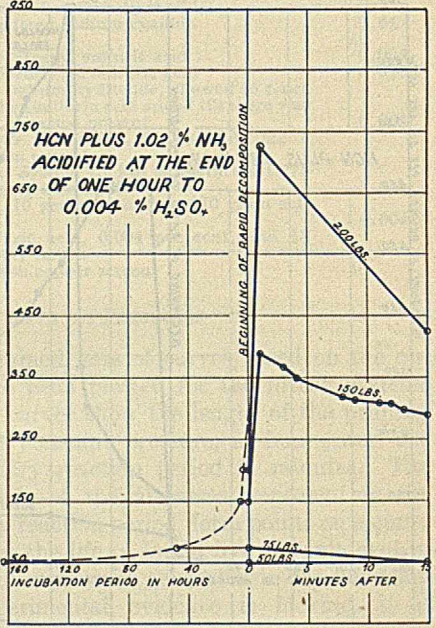
System 9



System 10



System 11



System 12

steeper and run higher in nearly all cases than with hydrocyanic acid alone or with ammonia. This additional rise may, however, be due to steam pressure from the water introduced.

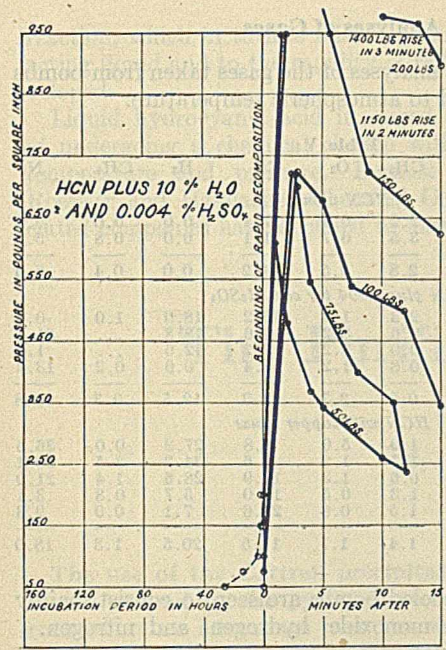
Comparing pure hydrocyanic acid with that containing 0.004 per cent sulfuric acid, it is seen that on the average the incubation period has been lengthened about 10 per cent by the introduction of the sulfuric acid and in general much lower final pressures are obtained. When the percentage of sulfuric acid is raised to 0.010 per cent the incubation period is lengthened by about 40 per cent and there are no high decomposition curves, probably owing to the combination of the ammonia with the sulfuric acid to form the solid ammonium sulfate.

When comparing the effect of metallic copper plus hydrocyanic acid with the behavior of pure hydrocyanic acid alone, the results are seen to be erratic. On the whole, the effect of copper as found here does not seem to be specially beneficial. When metallic copper (10 per cent) and sulfuric acid (0.004 per cent) are combined the final pressures are remarkably low, although the length of the incubation period is not much altered.

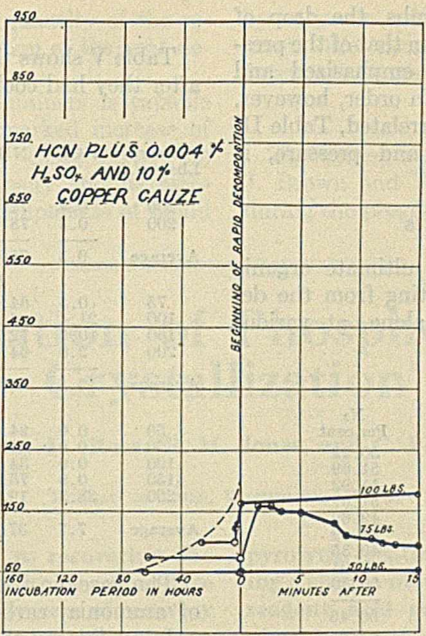
In the presence of 10 per cent of water, 0.004 per cent sulfuric acid does not seem to exert any beneficial effect, for the incubation period is not markedly lessened and the final curves are greater when the acid is used. This is perhaps due to insufficient acid to combine with all the ammonia formed, as when 0.010 per cent sulfuric acid is used with hydrocyanic acid alone the final pressure is markedly reduced.

Where a catalyst has been added and allowed to act for an hour at atmospheric temperature and sulfuric acid is then added, in 0.004 per cent excess, the acid exerts a marked stabilizing effect both in prolonging the incubation period over that found when the alkaline substance is used alone and in diminishing the rise of the final pressure.

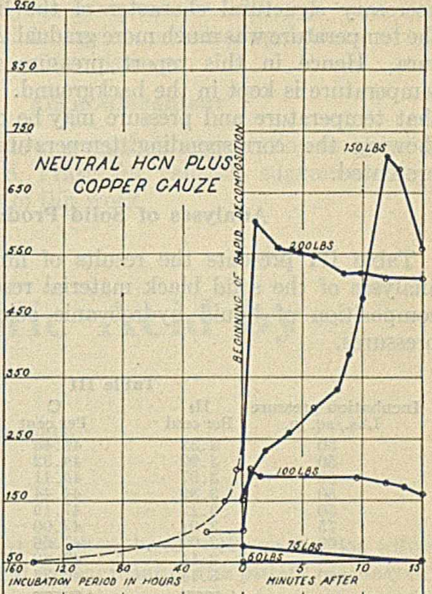
Conclusions—These experiments show in general that with hydrocyanic acid alone at elevated pressures there is a rather long preliminary period of comparatively slow reaction,



System 13



System 14



System 15

the length of which is governed by the initial pressure and the attendant temperature. This is followed by a much shorter period of violent reaction, during which the pressure and temperature rise very rapidly, then fall in a plain cooling curve. The introduction of hydroxyl ion shortens the preliminary period and increases the height of the curve representing the final reaction. The introduction of sulfuric acid retards the action started by hydroxyl ion and diminishes the height of the final reaction curves. This effect becomes very marked when copper and sulfuric acid are used together.

It is evident that at atmospheric temperature polymerization without rise of pressure is possible, but on the other hand, if decomposition starts and if the heat of the reaction is not balanced by the radiation from the container, the rise in pressure may be very sudden. Since pressures of over 1000 pounds per square inch have frequently been experienced in this work, there is danger of rupture of the container unless adequate precautions are taken to insure the stability of the material.

Table II

Pressure, Lbs./Sq. In.		Temperature, ° C.	
Incubation	Maximum	Incubation	Maximum
System 1—HCN alone			
50	98	80	101
75	255	80	217
100	730	120	235
150	692	122	257
200	715	146	281
System 2—HCN plus 0.24 per cent NH_3			
50	120	80	140
75	322	55	230
100	422	95	280
150	810	105	335
200	695	120	460
System 3—HCN plus 1.040 per cent NH_3			
50	85	70	85
75	140	90	115
100	680	105	365
150	730	115	405
200	820	160	335
System 4—HCN plus 3.860 per cent NH_3			
50	125	60	180
100	650	85	295
150	1000	95	340
System 5—HCN plus 0.57 per cent NaOH			
50	127	75	172
150	850	105	220
200	1050	125	210
System 6—HCN plus 0.64 per cent NaCN			
50	90	70	215
75	235	80	135
100	585	70	205
150	875	110	250
System 7—HCN plus 10 per cent H_2O			
50	95	70	100
75	610	80	255
150	825	110	300
200	900	120	230
System 8—HCN plus 0.004 per cent H_2SO_4			
50	55	75	80
75	315	82	125
100	120	100	240
150	285	110	175
200	860	120	340
System 9—HCN plus 0.010 per cent H_2SO_4			
50	90	70	90
100	170	110	160
150	325	120	125
200	355	125	270
System 10—HCN plus NaOH then 0.004 per cent H_2SO_4			
50	60	70	100
75	110	80	110
100	660	90	385
150	405	110	235
200	720	125	245
System 11—HCN plus NaCN then 0.004 per cent H_2SO_4			
75	170	85	110
100	190	100	120
150	790	125	320
200	700	120	290
System 12—HCN plus NH_3 then 0.004 per cent H_2SO_4			
50	95	75	95
75	95	85	115
150	390	125	200
200	630	125	215
System 13—HCN plus 10 per cent H_2O then 0.004 per cent H_2SO_4			
50	610	80	240
75	720	90	210
100	725	98	272
150	1100	115	345
200	1400	135	365
System 14—HCN plus Cu and 0.004 per cent H_2SO_4			
50	110	60	120
75	160	83	160
100	180	97	125
System 15—HCN plus 10 per cent Cu			
100	200	95	150
150	710	100	245
200	610	125	225

Data on Temperature

This investigation was projected as an inquiry into the pressure that might be expected from hydrocyanic acid under varying conditions of temperature and of impurities. During the investigation records of temperature were carefully kept, but it was found that the pressure rise was much more prompt and sharp than that of temperature; also, by virtue of the necessary structural character of the bombs, the drop of the temperature was much more gradual than that of the pressure. Hence in this report pressure is emphasized and temperature is kept in the background. In order, however, that temperature and pressure may be correlated, Table II, showing the corresponding temperature and pressure, is presented.

Analyses of Solid Products

Table III presents the results of nine ultimate organic analyses of the solid black material resulting from the decomposition of liquid hydrocyanic acid alone, at various pressures.

Table III

Incubation pressure Lbs./sq. in.	H_2 Per cent	C Per cent	N_2 Per cent
50	3.32	46.46	50.22
50	3.99	44.32	51.69
50	3.97	44.11	51.92
50	3.89	44.44	51.67
50	3.12	47.19	49.69
75	3.01	47.00	49.99
100	2.99	47.66	49.35
150	3.14	47.82	49.04
200	3.14	46.36	50.50
Average	3.40	46.15	50.45

It is seen that as the pressure rises the percentage of hydrogen in the solid decomposition product diminishes slightly. The same variation is seen in the case of the nitrogen, but the carbon content varies in the opposite direction.

If the percentages of the three elements shown above are compared with the percentages of the same elements as they exist in liquid hydrocyanic acid (hydrogen 3.71, carbon 44.44, nitrogen 51.85 per cent), it is observed that the hydrogen and nitrogen found by analysis have fallen off in percentage while the carbon has apparently increased. The reason for this is, as will be seen under Gas Analyses, that during the reaction ammonia has been formed and has entered the vapor phase, thus impoverishing the solid phase with respect to these two elements.

Table IV shows the average of all the analyses made for each system at the various pressures employed.

Table IV

System	SUBSTANCE ADDED TO LIQUID HCN	Per cent	H_2 Per cent	C Per cent	N_2 Per cent
1	None		3.36	46.00	50.63
2	NH_3	0.24	3.18	46.25	50.75
3	NH_3	1.040	3.45	45.94	50.93
4	NH_3	3.860	3.37	46.03	50.63
5	NaOH	0.57	3.48	44.59	51.92
6	NaCN	0.64	3.18	45.61	51.22
7	H_2O	10	3.54	43.23	53.11
8	H_2SO_4	0.004	3.22	45.69	51.08
9	H_2SO_4	0.010	2.98	46.16	50.85
10	1 gram NaOH then H_2SO_4	0.004 excess	3.20	46.77	50.03
11	1 gram NaCN then H_2SO_4	0.004 excess	3.27	46.10	50.63
12	1.775 grams NH_3 then H_2SO_4	0.004 excess	3.30	46.28	50.41
13	H_2O H_2SO_4	10 0.004	3.11	45.95	50.94
14	H_2SO_4 Cu	0.004 10	3.58	45.54	50.87
15	Cu	10	3.33	46.45	50.21

It may be seen that when copper is employed alone or with sulfuric acid the hydrogen percentage is higher than in the other cases.

All attempts to extract a crystalline compound from the black substance obtained in these experiments or in the material from other tests made at atmospheric temperature have given negative results. Attempts to detonate this black substance by percussion have failed, as have all endeavors to cause it to explode by heat. The material burns freely in the open air, but will not explode even when dropped into an iron tube that has been previously heated to redness.

No attempt was made to determine the yield of black material or of the gases in these experiments.

Analyses of Gases

Table V shows the analyses of the gases taken from bombs after they had cooled to atmospheric temperature.

Table V

Pressure Lbs./sq. in.	HCN	NH_3	CH_2	O_2	CO	H_2	CH_4	N_2
				HCN alone				
200	0.4	72.8	2.2	0.4	17.4	0.0	0.0	6.8
200	0.3	78.4	3.5	0.7	11.1	0.0	0.8	5.3
Average	0.3	75.6	2.8	0.5	14.2	0.0	0.4	6.0
				HCN plus 0.004 per cent H_2SO_4				
75	0.5	64.2	2.3	1.2	12.2	18.0	1.0	0.6
100	21.4	6.6	0.6	8.2	12.6	18.8	...	31.8
150	0.0	72.6	0.0	0.2	13.2	12.6	...	1.4
200	2.0	64.6	0.8	1.2	17.4	0.6	0.2	13.2
Average	5.8	52.0	0.9	2.7	11.3	12.5	0.3	11:8
				HCN with copper gauze				
50	0.0	24.6	1.9	5.0	4.8	27.2	0.0	36.5
50	0.0	34.7	1.7	1.2	4.6	34.2	3.5	20.1
100	0.0	34.2	0.6	1.3	12.9	28.6	1.4	21.0
150	0.0	75.6	1.3	0.5	13.0	5.7	0.8	3.1
200	38.3	19.5	1.5	0.8	22.6	7.1	0.9	9.3
Average	7.7	37.7	1.4	1.7	11.5	20.5	1.3	18.0

The gases in the cooled bombs are seen to consist mainly of ammonia, carbon monoxide, hydrogen, and nitrogen.

In explaining the presence of oxygen and of carbon monoxide it should be stated that the volumetric capacity of the thimble was 810 cc., the volume of hydrocyanic acid placed therein was 250 cc., thus leaving 650 cc. of gas space after the liquid was introduced. It required about 25 minutes to seal a bomb after the liquid had been inserted, and during this time the interior of the bomb communicated with the atmosphere by a 6-mm. (1/4-inch) hole through which some gaseous hydrocyanic acid passed as the temperature was approximately 25° C. During this time some of the air originally in the thimble was driven off with the escaping gaseous hydrocyanic acid, but an analysis of the gas in the bomb at the end of the sealing period showed that the air was not completely expelled, as shown herewith:

HCN, 60.5 per cent by volume; O_2, 8.7 per cent; N_2, 30.8 per cent

Thus, there were about 60 cc. of oxygen and 197 cc. of nitrogen in the bomb when sealed off from the air. This yielded the oxygen for the formation of the carbon monoxide and left some oxygen free. The nitrogen from air probably accounts entirely for the free nitrogen found in the bombs.

Only the general character of the gaseous constituents can be learned from the foregoing analyses. No definite relation is seen between the amounts of the same compounds and the pressure, nor is there any apparent relation between the variety of the compounds and the pressure.

No great effort was made to establish the ratio between the volume of gas formed and the quantity of the solid product. Since it was observed that the volume of the solid black product formed was greater than that occupied by the original liquid and since no loss took place from the closed system, it is evident that the weight ratio of gaseous products to the solid or to the original liquid must have been very small. Evidently, both by analysis of the solid product and by estimation of the gaseous volume, the actual amount of breaking up or rupturing of the hydrocyanic acid molecule was rather small and polymerization rather than decomposition prevailed in the main.

Conclusion

It is believed from a study of the whole problem that the explosions are due, not to spontaneous rupturing of the hydrocyanic acid molecule, but to the pressure of the gases formed by hydrolytic decomposition of the liquid hydrocyanic acid. Consequently, the pressure to be expected in a closed container is dependent on the rapidity and the extent of this reaction, which in turn is related to the quantity of the reacting liquid and to the rapidity of radiation of the heat developed.

Liquid hydrocyanic acid in closed containers is capable of undergoing a chemical change with marked increase of temperature and pressure. Because of these facts, the Roessler and Hasslacher Chemical Company and its associated companies have declined to make shipments of liquid hydrocyanic acid by common carrier, although such shipments are permissible under present regulations of the Interstate Commerce Commission.

Acknowledgment

The writers wish to express their appreciation to Mortimer J. Brown and F. S. Pratt, for valuable suggestions given during the progress of this work.

The Purification of Phosphoric Acid by Crystallization[1]

By Wm. H. Ross, R. M. Jones, and C. B. Durgin

Bureau of Soils, Washington, D. C.

The use of the Cottrell precipitator in recovering the fumes evolved in the pyrolytic treatment of phosphate rock offers an advantage over the wet system of recovery in that it may be adjusted to give directly an acid solution of such concentration that the greater part of it crystallizes on cooling to a mass of orthophosphoric acid crystals. On centrifuging the crystals and recrystallizing, a large proportion of the impurities pass into the mother liquor, leaving a crystalline product of relatively high purity as compared with the original acid. The process of crystallization is accordingly suggested as a means of increasing the value of a portion of the product recovered in the pyrolytic treatment of phosphate rock, as well as affording a simple method for increasing the purity of analytical reagent acid such as that prepared from elementary phosphorus.

The physical properties of anhydrous and hydrated phosphoric acid crystals are compared and the conditions best adapted to purification by crystallization are described. Curves are given which show the solubility of phosphoric acid at different temperatures, and the percentage yield of crystals given by supersaturated solutions of different concentrations.

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IN a previous paper[2] an account is given of a preliminary investigation on the preparation of phosphoric acid from phosphate rock by the volatilization method. Use was made of an electric furnace of 25 kilowatt capacity operated by a three-phase alternating current at 50 to 100 volts. The charge consisted of a mixture of 6 parts of phosphate rock, 3 of sand, and 1 of coke. The scrubbing tower method was first used for the collection of the acid, but as this proved unsatisfactory it was later replaced by a Cottrell precipitator. This system was found to offer many advantages over the wet system formerly used and it is now applied commercially in the recovery of volatilized phosphoric acid.

Preparation of Volatilized Phosphoric Acid

In an open furnace such as that used in the experiments outlined, the evolved phosphorus is oxidized within the furnace and passes to the collecting system in the form of voluminous white fumes of phosphorus pentoxide. Owing to its hygroscopic nature this at once reacts with the moisture in the air with which it comes in contact in passing to the precipitator and is precipitated in the form of a solution of orthophosphoric acid.

In continuing these experiments it was found that the concentration of the acid collected could be very easily regulated by adjusting the flow of air through the furnace or by changing the temperature at which precipitation takes place. The temperature at which the acid is precipitated depends on the amount of heat which the gases lose by radiation in passing to the precipitator. When this is so regulated that the temperature of precipitation is above 100° C. an acid is collected of such concentration that the greater part of it crystallizes on cooling to a mass of orthophosphoric acid crystals.

Note—When sufficient water is added to phosphorus pentoxide to correspond to orthophosphoric acid a sirupy solution of metaphosphoric acid is obtained, which will not crystallize at first and will only partially crystallize on standing for several months. It was, therefore, unexpected that the pentoxide produced in the smelting of phosphate rock should change quantitatively into the ortho acid during the short interval required for the fumes to pass from the furnace to the precipitator, and no explanation is known for the acceleration of the reaction.

On centrifuging these crystals a large proportion of the impurities originally present in the acid pass into the mother liquor leaving a crystalline product that is relatively pure as compared with the original acid.

Preparation of Sirupy Phosphoric Acid

The C. P. phosphoric acid ordinarily found on the market is also prepared by the volatilization method, but with the marked variation that the phosphorus is volatilized in a nonoxidizing atmosphere and is therefore recovered in the elementary form rather than as a solution of phosphoric acid. The phosphorus is subsequently converted to phosphoric acid by oxidation with nitric acid, following which the excess of nitric acid and its reduction products are eliminated by heating and concentration.

The acid prepared in this way is ordinarily marketed as a sirupy liquid having a concentration of 85 to 90 per cent H_3PO_4. The more concentrated acid, such as the 90 per cent grade now marketed by the Mallinckrodt Chemical Works, is supersaturated at ordinary temperatures and will partially crystallize when inoculated with a hydrated crystal. Acid of 85 per cent concentration will not crystallize directly at normal temperatures, but it may be made to crystallize readily by cooling below 10° C. and inoculating with a hydrated crystal, or by concentrating below 100° C. to a specific gravity of about 1.85 and inoculating with a crystal of the anhydrous acid.

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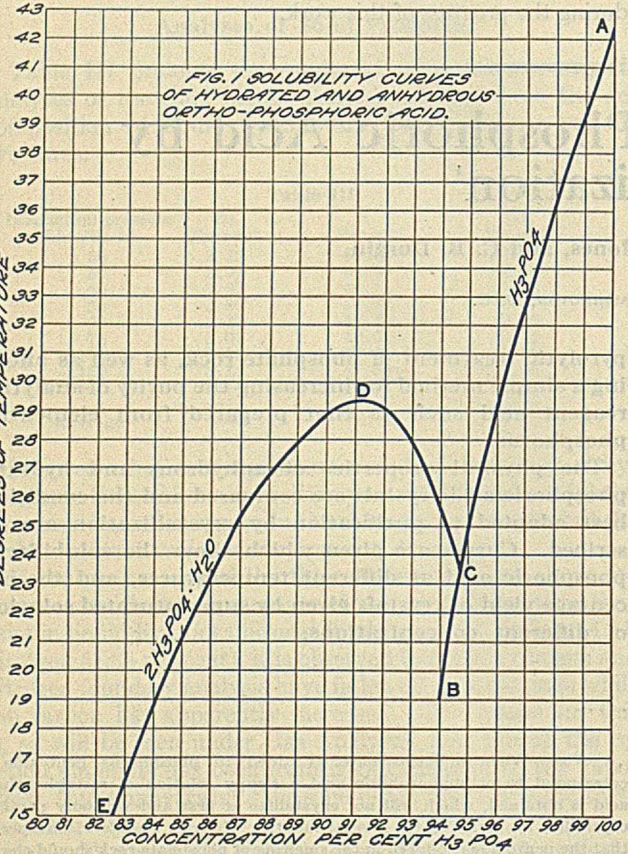
[1] Received June 25, 1925.

[2] Ross, Carothers, and Merz, This Journal, 9, 26 (1917).

A study was accordingly undertaken of the crystal properties of phosphoric acid with a view to the possibility of applying the process of crystallization (1) as a simple laboratory method for the further purification of the ordinary reagent acid; and (2) as a method for the purification of commercial phosphoric acid prepared by the volatilization process.



Purification of Sirupy Phosphoric Acid

A chemical method for the preparation of phosphoric acid of a higher degree of purity than the ordinary C. P. acid is described by Abbott and Bray.[3] The process of crystallization, however, can be applied more conveniently and insures a purer product. For best results the acid should be concentrated at a temperature below 100° C. until it reaches a specific gravity of about 1.85 20°/20° C. The solution is then cooled below 40° C., inoculated with a crystal of the anhydrous acid, allowed to stand in a closed vessel until crystallization is complete, and the mother liquor then separated from the crystals by centrifuging in a closed porcelain-lined centrifuge. The crystals recovered in this way are melted at a temperature of about 50° C., sufficient water is added to bring to a specific gravity of 1.85 as before, the solution again inoculated with a crystal, and the process repeated two or three times. The crystals may be dried by allowing to stand for several weeks over phosphorus pentoxide.

The ordinary sirupy acid may also be further purified without preliminary concentration by cooling to 10° C. or lower, inoculating with a hydrated crystal, allowing to stand until crystallization is complete, and centrifuging at a temperature below normal. The hydrated crystals differ from the anhydrous in that they exhibit a marked tendency to cake, and their use affords the further disadvantage that they can only be conveniently handled in cool weather or where refrigeration facilities are available. Hydrated crystals ($2H_3PO_4.H_2O$) may be prepared free from adsorbed moisture by adding the proper amount of water to a weighed portion of fused anhydrous phosphoric acid, cooling below 29° C., and inoculating with a hydrated crystal.

The purity and freedom from adsorbed moisture of the anhydrous and hydrated crystals prepared by the methods outlined were shown (1) by analysis, (2) by the very sharp melting points of the crystals, and (3) by their rate of formation.

ANALYSIS OF PHOSPHORIC ACID—The analysis of high-grade phosphoric acid was made most conveniently and accurately by titrating with standard alkali solution until the color given by phenolphthalein as indicator exactly matched that of another solution of similar volume, and which contained approximately the same quantity of indicator and of phosphoric acid in the form of disodium phosphate.

MELTING POINTS OF PHOSPHORIC ACID—In Table I are given the melting points of phosphoric acid crystals as reported by different investigators. The results show that the values obtained for the crystals prepared in this work agree closely with those reported by Smith and Menzies,[4] but differ considerably from those given by Thomsen,[5] Berthelot,[6] and Joly.[7]

Table I—Melting Points of the Crystal Forms of Phosphoric Acid

Crystal composition	Thomsen	Berthelot	Joly	Smith and Menzies	Authors
H_3PO_4	38.6	41.75	...	42.30	42.35
$2H_3PO_4.H_2O$	...	...	27.0	29.35	29.32

RATE OF CRYSTALLIZATION OF PHOSPHORIC ACID—According to statements appearing in the literature,[4,8] hydrated phosphoric acid crystallizes spontaneously with no noteworthy supercooling, whereas the anhydrous acid crystallizes slowly with much greater difficulty and changes with loss of water at 200° to 300° C. to pyrophosphoric acid.

In the course of this work little difference was observed in the tendency of the two crystal forms of the acid to crystallize spontaneously. The fused anhydrous acid and a solution corresponding to the hydrate were frequently cooled to almost 0° C. before spontaneous crystallization occurred and both may be kept in a closed vessel indefinitely without crystallization. Inoculation with the corresponding crystal suffices, however, to start crystallization immediately and at a rate in excess of that of many well-known substances.[9] The values found for the rate of crystallization of both the anhydrous and hydrated acid amounted to 33.3 cm. and 2.6 cm. per minute, respectively, at 20° C.

The temperature to which phosphoric acid is subjected before crystallizing has a marked effect on the rate at which crystallization takes place. This rate rapidly diminishes as the temperature is raised above 100° C. and no crystallization will occur in an acid that has been maintained for some time at 130° C. or above. This shows that orthophosphoric acid decomposes at a temperature considerably below 200° C., and that the concentration of acid intended for crystallization should be made at 100° C. or below.

Solubility of Phosphoric Acid

The solubility curve *AB* of anhydrous phosphoric acid and the portion *CDE* of the curve of the hydrated acid above 15° C. are represented in Figure 1. By use of these curves the amount of acid that will be deposited on crystallizing from a solution of known concentration and temperature may be readily estimated. Thus, at 24° C., for example, no crystallization will

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[3] *J. Am. Chem. Soc.*, **31**, 729 (1909).

[4] *J. Am. Chem. Soc.*, **31**, 1183 (1909).

[5] *Ber.*, **7**, 997 (1874).

[6] *Ann. chim. phys.*, [5] **14**, 441 (1878).

[7] *Compt. rend.*, **100**, 447 (1885).

[8] Ostwald, "Principles of Inorganic Chemisrty," 4th ed., p. 391.

[9] Tammann, "Kristallisieren und Schmelzen."

occur below a concentration of 86.3 per cent. Above this concentration a hydrated crystal will induce partial crystallization in the solution, the proportion increasing up to 91.6 per cent, when the whole mass becomes solid. With still greater concentrations partial crystallization again occurs until at a concentration of 94.6 per cent no crystallization follows inoculation with either hydrated or anhydrous crystals. This holds true up to 94.8 per cent acid. Above this concentration partial crystallization will follow inoculation with an anhydrous crystal, the amount deposited increasing up to 100 per cent acid, when it crystallizes to a solid mass.

The curves also show that at 24° C. no crystallization will take place when a 94.8 per cent solution is inoculated with either a hydrated or anhydrous crystal or both, but that the whole mass becomes solid when the temperature of the solution is lowered one degree or more.

The quantity, Q_A, of anhydrous crystals that will be deposited at a given temperature per 100 grams of a supersaturated solution is given by the equation:

$$Q_A = \frac{100(S - s)}{100 - s}$$

when S and s are the percentages of phosphoric acid in the supersaturated and saturated solutions, respectively. The corresponding equation for the hydrated crystals is

$$Q_H = \frac{100(S - s)}{91.6 - s}$$

If Q_A and Q_H are desired in percentages of the total acid present rather than in percentages of the supersaturated solutions, the foregoing expressions must then be multiplied by the factor $100/S$.

The values of s for different temperatures are given in Table I of a previous publication[10] and are shown graphically in Figure 1. At 25° C., for example, the value of s for the anhydrous acid is 95.00 per cent. It may thus be calculated that the crystals deposited from, say, a 97.5 per cent solution of phosphoric acid will amount to 50 per cent of the weight of the solution.

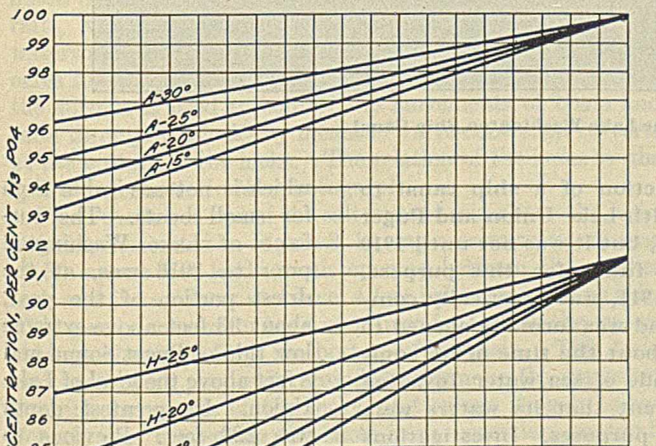

FIG. 2

Values of Q_A and Q_H for different concentrations and temperatures may also be determined from the curves in Figure 2, of which curves $A - 15°$ to $A - 30°$ show the quantities of anhydrous crystals deposited from solutions of different concentrations at temperatures ranging between 15° and 30° C., while curves $H - 5°$ to $H - 25°$ give the corresponding data for hydrated crystals. Thus the abscissa 97.5, cutting the curve $A - 25°$ at ordinate 50 shows, as before, that the crystals deposited from a 97.5 per cent solution of phosphoric acid will amount to 50 per cent of the weight of the solution. The curves also show conversely the extent to which phosphoric acid solutions must be concentrated to yield any desired proportion of crystals.

Purification of Commercial Acid

The most apparent impurities in volatilized phosphoric acid are hydrofluoric acid and suspended material which is carried over mechanically in the gases. Solutions which are saturated with respect to the hydrated crystals can be readily filtered, but those which are sufficiently concentrated to yield anhydrous crystals are too viscous to be filtered by ordinary methods. If the solutions are crystallized without filtering, suspended material is carried down with the crystals and the purity of the latter is correspondingly reduced. It has been found, however, that the suspended matter will slowly settle out on standing and that the rate at which this takes place is rapidly increased if the temperature of the acid is maintained between 50° and 90° C. One of three procedures may accordingly be followed in the crystallization of volatilized acid:

(1) The acid is kept in a warm place until it settles clear and the specific gravity adjusted to about 1.85. The solution is then decanted, cooled to normal temperature or below, inoculated with an anhydrous crystal, and the procedure continued as described in the crystallization of analytical reagent acid. If it is desired to reduce some of the impurities, such as fluorine, lead, and arsenic, in relatively greater proportion than the others, the acid may be treated before standing with the appropriate quantity of suitable precipitating reagents, such as sodium silicate for fluorine[11] and sodium sulfide for lead and arsenic. The suspended and precipitated materials are then allowed to settle out as before, the clear acid decanted off, adjusted to a specific gravity of 1.85, and the purification completed by crystallization.

(2) The acid is diluted to a specific gravity of 1.75, treated chemically as described in (1), filtered through sand, concentrated to a specific gravity of 1.85, and inoculated with an anhydrous crystal.

(3) The acid is diluted to a specific gravity of 1.75, treated chemically, filtered, cooled below 20° C., and inoculated with a hydrated crystal.

Table II—Composition of Crude and Crystallized Phosphoric Acid

	PERCENTAGE COMPOSITION ON BASIS OF 90 PER CENT H_3PO_4					
	Crude	First Crop of Crystals		Chemically Treated	First Crop of Crystals	
CONSTITUENTS	Acid	Anhydrous	Hydrated	Acid	Anhydrous	Hydrated
Sodium	0.26	0.05	0.17	0.17	0.08	0.12
Potassium	0.51	0.06	0.22	0.35	0.07	0.13
Calcium	0.16	0.00	0.04	0.01	0.00	0.00
Iron	0.052	0.013	0.021	0.071	0.009	0.036
Aluminium	0.06	0.00	0.03	0.04	0.00	0.03
Manganese	0.002	0.00	0.001	0.005	Trace	0.002
Chlorine	Trace	0.00	0.00	0.00	0.00	0.00
Sulfate	0.03	0.00	0.00	0.22	0.00	0.04
Fluorine	0.07	0.00	0.02	0.02	0.00	0.00
	PARTS PER MILLION					
Lead	189	34	79	21	9	8
Arsenate	215	6	28	2	Trace	Trace

The hydrated crystals differ from the anhydrous in that they cake to a very marked degree and cannot be applied as efficiently as the latter in the purification of the acid. This is indicated by the results given in Table II, which show the extent to which the impurities in two commercial grades of acid were reduced by one crystallization. Both samples were allowed to stand before analyzing until suspended material had settled and one was treated chemically while standing, to reduce fluorine, lead, and arsenic. Four crystallizations of each acid gave a product which did not contain a sufficient quantity of any impurity to be identified by chemical tests.

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[10] Ross and Jones, *J. Am. Chem. Soc.*, **47**, 2165 (1925).

[11] Carothers and Gerber, U. S. Patent 1,487,205.

The Control of Sea Water Flowing into the Lake Washington Ship Canal[1]

By E. Victor Smith and Thomas G. Thompson

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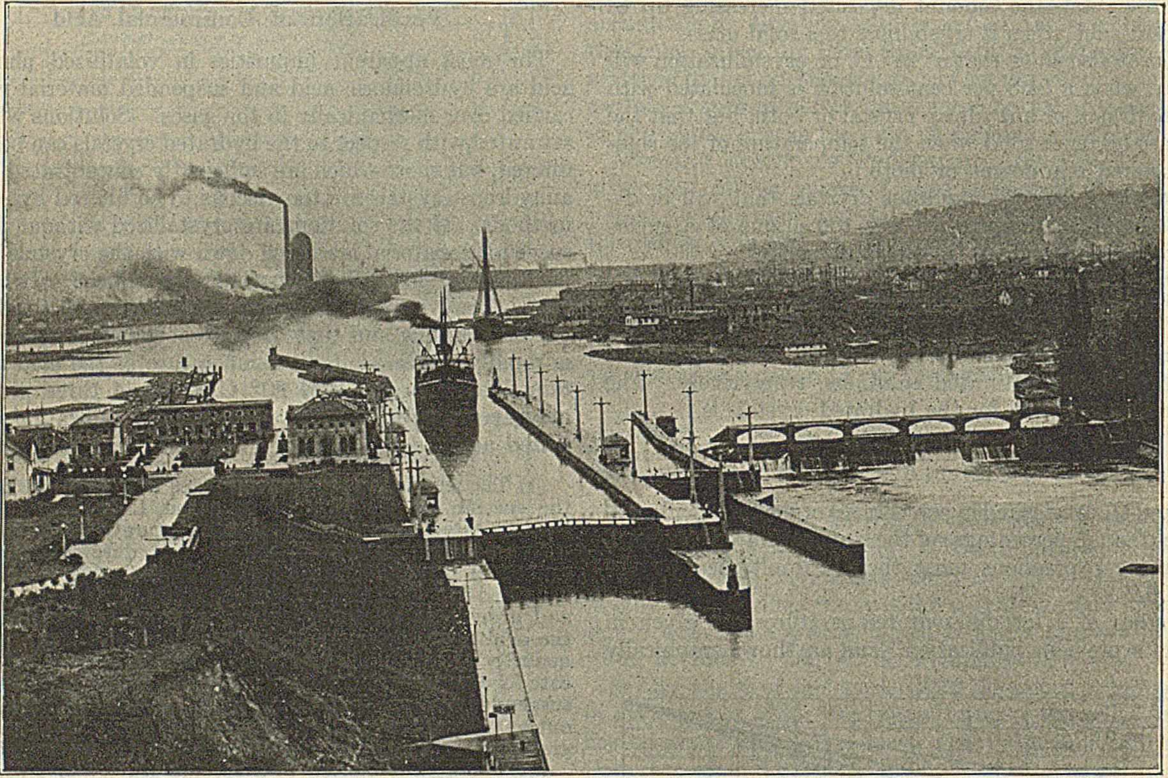

Locks and Spillway Looking up the Lake Washington Ship Canal

Agitation for the construction of a ship canal to connect Lake Washington with Lake Union and Puget Sound began as early as 1854, but it was not until 1910 that Congress appropriated funds for this purpose. The construction began in 1911, was practically completed in September, 1916, and was formally opened to shipping on July 4, 1917. About the time of its completion, complaints were made of sea water invading Lake Union to such an extent that its waters were rendered unfit for industrial purposes. Investigations were begun by the authors at this time and have been continued up to the present. A summary of the results obtained is given in this paper.

IN ORDER to understand the relation of this canal to the bodies of water that it connects, it may be well to describe briefly the geographical situation. The accompanying map (Figure 1) shows the location of the canal in Seattle and its relation to Puget Sound, Lake Union, and Lake Washington. Puget Sound is an arm of the Pacific Ocean, which extends a considerable distance into the State of Washington and covers an area of about 2000 square miles. Lake Washington lies nearly parallel to the eastern shore of Puget Sound and at a distance varying from 2 to 5 miles. It is 19 miles long by about 2 miles wide, has an area of 39 square miles, and is the drainage basin for 182 square miles of territory, which includes that drained by Lake Sammamish. The latter is a long lake several miles to the east of Lake Washington, lying nearly parallel to it, has an area of 7.5 square miles, and drains 60 square miles of territory. The two lakes are connected by the Sammamish River, which is not navigable even for small boats. The surface of Lake Washington prior to 1916 was, at the driest portion of the year, about 33 feet above extreme low tide of Puget Sound and 8 feet above the level of Lake Union. Its greatest depth was 223 feet. Previous to 1886 the only outlet was the Black River, which issued from the southern extremity of the lake. This outlet no longer exists. Lake Union lies between Lake Washington and Puget Sound. It has an area of 905 acres, of which 499 cover areas deeper than 25 feet. The maximum depth as charted is 50 feet. A territory of approximately 6 square miles drains into this lake, but with the growth of Seattle this drainage has been greatly reduced; much water which otherwise would flow into the lake now finds its way to Puget Sound by means of the city sewers. The surface of the lake is about 25 feet above extreme low tide and 7 feet above extreme high tide. Before the cutting of the canal the lake was drained by a small stream following approximately the present waterway between the lake and Puget Sound.

Previous to the construction of the locks, Salmon Bay,

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[1] Presented before the Division of Water, Sewage, and Sanitation at the 86th Meeting of the American Chemical Society, Ithaca, N. Y., September 8 to 13, 1924. Received May 25, 1925.

now a part of the canal, was an estuary of Shilshole Bay, which in turn is an arm of Puget Sound.

The Lake Washington Ship Canal has increased the harbor facilities of Seattle and made available a large fresh-water basin in which ocean vessels may lie. The total length of the canal, from deep water of Puget Sound to deep water of Lake Washington, is nearly 8 miles. Cutting and dredging was necessary for the greater part of the distance, that portion of Lake Union shown in Figure 1 between Stations 6 and 10 being the only part that did not require dredging. After the cut between Lake Washington and Lake Union was completed, the surface of Lake Washington was lowered 8 feet. It is now level with Lake Union.

Lock Control of Sea Water

At the lower end of Salmon Bay a lock system has been constructed for the passage of ships and for the control of water. Above the locks the water is maintained at a nearly constant level, whereas the level below is subject to tidal variations. Between the locks and Lake Union the depth of the water in the channel is 31 feet, except that an irregularly shaped "salt water basin" has been dredged immediately above the locks. This basin is about 1600 yards long, upward of 200 feet wide, and varies from 32 to 50 feet in depth. In Lake Union the water in the channel varies between 37 and 50 feet in depth, in Portage Bay and Union Bay the depth is 26 feet, and in the cut between these two bays it is 28 feet. Figure 2 shows the variation in depth from the locks to deep water in Lake Washington.

There are two locks side by side, the larger of which is 825 feet long, 80 feet wide, and at high tide has a depth of 43 feet of water; the smaller lock is 150 feet long, 30 feet wide, and at high tide has a depth of 30 feet. The larger one is, of course, for the use of vessels that cannot be accommodated by the smaller lock. It is also extensively used by log rafts, which are towed to the sawmills situated along the waterway. South of the smaller lock is a spillway, which cares for a portion of the surplus water. The remainder of the surplus is used to control the movements of boats and rafts through the locks by means of valve-controlled culverts at the bottom of the locks. The relation of the locks to the spillway is shown in the photograph.

From the lower end of the salt water basin above the locks a drain, illustrated in Figure 3, having a cross-sectional area of 30 square feet leads to an opening between the smaller lock and the spillway at a level 4 feet below that of high tide. This gives a maximum head of 11 feet for forcing the waters through the drain from the bottom of the basin. This drain and basin were purposely provided to remove the sea water entering by means of the locks, and return it again to the Sound, thus preventing the lakes from becoming contaminated. This is an innovation in the construction of canals connecting bodies of fresh water with the sea. It was suggested by the engineers of the United States Army as the result of experiences in the operation of the Panama Canal. The so-called climbing of sea water into the fresh water bodies of the Panama Canal has been recently described by Kirkpatrick.[2]

This tendency of salt water to "climb" above sea level was known to the Egyptians and Persians. It was advanced by Urco in 610 B. C. as one of the objections against the completion of the canal connecting the Nile River with the Red Sea.[3]

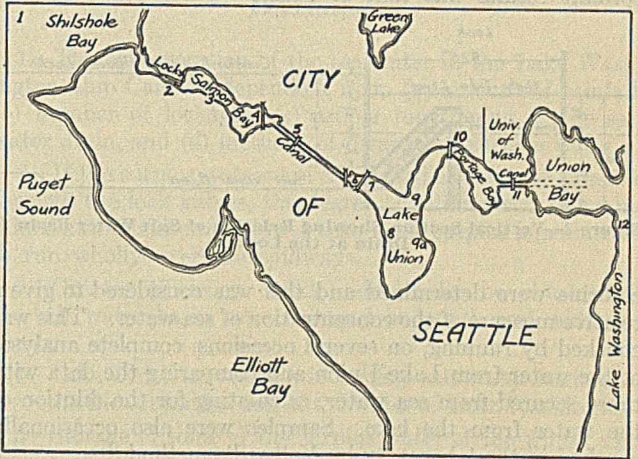

Figure 1—Map Showing Lake Washington Ship Canal

During lockages in the Lake Washington Ship Canal a strong current of sea water flows from the bottom of the locks up the canal into the salt water basin. There is an equal countercurrent of fresh water at the surface. This condition is due to the fact that sea water, having the greater density, tends to seek the lower levels. The failure of the drain to function, or a heavy lockage during the dry season, will cause the flooding of the salt water basin by the sea water to such an extent that a decided current of sea water will flow into the lower levels of Lake Union. The lake behaves as a secondary basin and prevents the flow of sea water into Lake Washington. The sea water that enters Lake Union tends to distribute itself throughout the waters of the lake owing to natural diffusion, disturbances caused by currents, changes in temperature, and the passage of boats. However, the greater bulk of the sea water will remain below the 40-foot level. This is demonstrated by the data given below.

Methods of Sampling

Two methods of sampling the waters for analysis were used, both of which gave practically identical results. The device utilized more commonly was a reversing water bottle of the Eckman type with attached reversing thermometers. The other apparatus consisted of a marine pump with 50 feet of 0.75-inch garden hose graduated in feet. Sampling with this apparatus was more tedious and was only operated to check doubtful results and for collection of plankton.

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[2] *Eng. News-Record*, **92**, 935 (1924).

[3] Rawlinson, "History of Herodotus," Vol. III, p. 28.

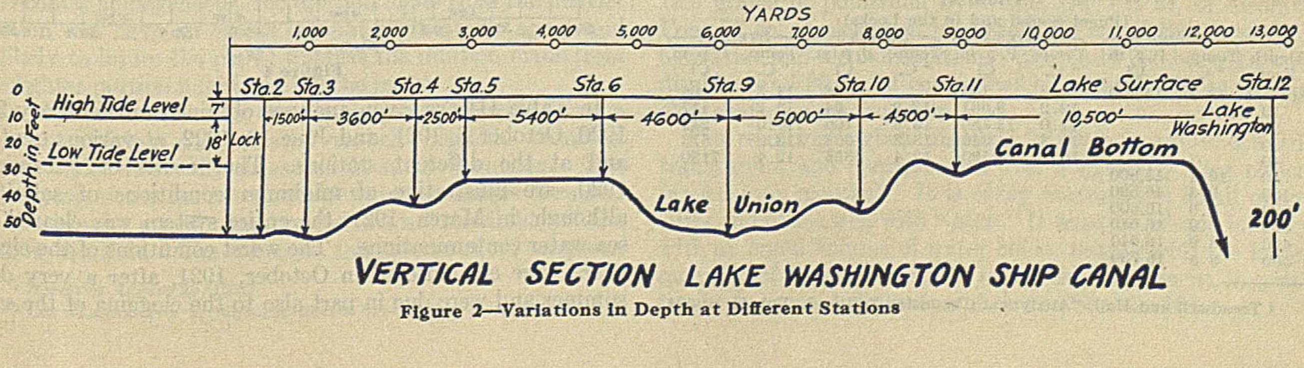

Figure 2—Variations in Depth at Different Stations

Methods of Analysis

For determining the quantity of chlorine present in the water, various methods were studied. Attention was given to conductivity and specific gravity methods, but results of considerable variation were obtained, owing to differences in temperature and contamination from industrial plants along the waterway. The method that gave the most concordant results was that of Mohr.[4] Parts per million of chlorine were determined and this was considered to give a relative measure of the concentration of sea water. This was checked by running, on several occasions, complete analyses of the water from Lake Union and comparing the data with those secured from sea water, calculating for the dilution of the water from the lake. Samples were also occasionally checked in the laboratory by Volhard's method.

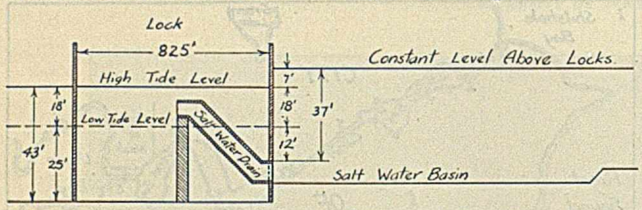

Figure 3—Vertical Section Showing Relation of Salt Water Basin to Drain at the Locks

As from one hundred to two hundred analyses were necessary for each study, it was almost impossible to collect samples and transport them to the laboratory. Accordingly, an improvised laboratory was set up on the yacht "Orcas," which was furnished by the United States Army. As fast as the samples were brought aboard they were analyzed by pipetting off 100 ml. and titrating. Two standard solutions of silver nitrate of different concentrations were used, one for water of low salinity and the other for water of high salinity. Possible errors due to temperature changes were within the ordinary experimental error, there seldom being a variation greater than 7° C. in the temperature of the water throughout the entire year. In some cases, as at the bottom of Lake Union, considerable quantities of hydrogen sulfide were encountered, which resulted from the hydrolysis of waste products formerly thrown into the lake by a large gas plant situated on the shore. Such samples were further treated in the regular laboratory.

Salinity Variation in the Locks

The chlorine content of the waters at various depths in and near the locks is shown in Table I. The samples from which the data were secured were all collected the same forenoon. In Series 1 are given the parts per million of chlorine obtained from water taken at varying depths from Puget Sound (Station 1) about 1 mile from the entrance to the locks. The effect of drainage waters from the land into the sea is distinctly indicated in this series of analyses, as a concentration of chlorine on the surface is decidedly lower than that secured at greater depths.

Table I—Parts per Million of Chlorine at Various Depths at Stations 1 and 2

(Puget Sound and in the Locks)

	SERIES 1		SERIES 2		SERIES 3		SERIES 4	
Depth Feet	Temp. ° C.	P. p. m. Cl	Temp. ° C.	P. p. m. Cl	Temp. ° C.	P. p. m. Cl	Temp. ° C.	P. p. m. Cl
Surface	13.3	14,450	14.2	144		68	14.5	66
10			12.2	8,681	13.9	64	14.2	117
20			11.0	13.760	13.6	106	14.0	244
30			10.8	14,340	13.3	663	13.0	573
40			10.7	14,520	12.4	5355	12.4	7180
50	10.4	15,900						
100	9.5	16,590						
200	8.9	16,600						
300	8.9	16,640						
400	8.9	16,640						
500	8.8	16,730						

The collection of samples the data of which are shown under Series 2 was started 10 minutes after the large lock (Station 2) had been opened to the sea and during an ebbing tide. The samples were taken at a point midway between the two lock gates. The data indicate how completely the sea water replaces the fresh water in the locks when they are opened to the sea.

Immediately after securing the samples of Series 2, those of Series 3 were obtained on the fresh water side of the upper lock gate. Upon completion of this operation the lower gate was closed to the sea, the water in the locks raised to the level of the canal, and the upper gate opened. As soon as the whirling of the waters in the locks had ceased, samples were taken from the same position as that from which those of Series 2 had been secured. The results, given under Series 4, demonstrate that the sea water had largely disappeared by flowing into the basin above the locks. The sample taken from the bottom of the lock was the only one showing a high degree of salinity.

Flow of Sea Water into the Canal and Lakes

No attempt will be made to show all the data secured during the eight years that this investigation has been under way. From those presented in Table I it is obvious that the waters of the canal near the locks undergo constant change. However, as the distance from the locks increases the analyses of the water indicate fairly constant conditions. For example, in Lake Union the change is relatively slow, so that remarkably constant results may be obtained from month to month, especially at the greater depths. Samples were taken at the different stations, indicated in Figure 1, at every 10 feet. Table II gives the relative distances of the respective stations from the locks.

Table II

Between stations	Distances between the various stations Feet	Distance from locks (Station 2) Feet
1 and 2		
2 and 3	1,500	1,500
3 and 4	3,650	5,150
4 and 5	2,500	7,650
5 and 6	5,400	13,050
6 and 7	1,650	14,700
7 and 9	3,000	17,700
9 and 10	5,000	22,700
10 and 11	4,500	27,200
11 and 12	10,500	37,000

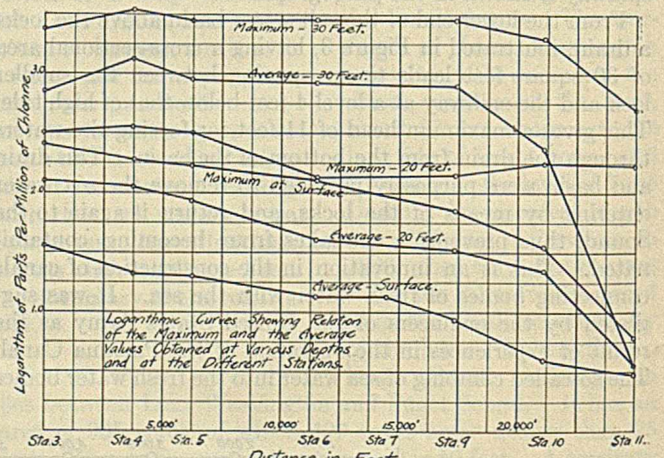

Figure 4

In Table III are given analyses obtained on February 21, 1920, October 8, 1921, and June 10, 1922, at various depths and at the different stations. The results of February, 1920, are illustrative of minimum conditions of salinity, although, in March, 1921, the entire system was cleared of sea water contaminations. The worst conditions of the eight years were encountered in October, 1921, after a very dry summer and were due in part also to the clogging of the salt

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[4] Treadwell and Hall, "Analytical Chemistry," 6th ed., Vol. II, p. 604.

water drain for a time by a sunken log. This shows very well the ease with which the waters of the canal and lakes might have become contaminated if proper control had not been provided by the army engineers. The data for June, 1922, indicate the effect of drainage resulting from winter rains and spring freshets. In Figure 4 the logarithms of the parts per million of chlorine for the maximum and average conditions are plotted for the various depths at the different stations along the waterway.

Table III—Parts per Million Chlorine, Showing Maximum and Minimum Conditions Obtained at Various Depths and Different Stations

Station	Date tested	Depth in Feet							
		0	10	20	30	32	40	45	50
3	Feb. 20, 1920								
	Oct. 21, 1921	244	237	310	2315		7800	9075	
	June 22, 1922	10	9	33	325				
4	Feb. 20, 1920	16	16	26	55	130			
	Oct. 21, 1921	193	198	360	3555				
	June 22, 1922	6	8	13	600				
5	Feb. 20, 1920	16	15	16	14				
	Oct. 21, 1921	169	171	315	2920				
	June 22, 1922	3	4	7	75				
6	Feb. 20, 1920	9	12	15	14				
	Oct. 21, 1921	128	137	135	2940	3125			
	June 22, 1922	3	3	4	20	28			
9	Feb. 20, 1920	7	9	9	9		4149	5040	
	Oct. 21, 1921	70	111	145	2875		4710	5830	
	June 22, 1922	4	3	5	10		420	3995	
10	Feb. 20, 1920	3	3	3	3		3		
	Oct. 21, 1921	36	37	178	1985		2507		
	June 22, 1922	3	3	3	4		4		
11	Feb. 20, 1920	3	3	3	3				
	Oct. 21, 1921	6	14	173	505				
	June 22, 1922	3	3	3	3				
12	Feb. 20, 1920	3							3
	Oct. 21, 1921	3							3
	June 22, 1922	3							3

Rather peculiar results for maximum conditions at depths of 20 feet and 30 feet and for average conditions at 30 feet are indicated by the curves in Figure 4 at Stations 3 and 4. The former, being nearer the locks, should show a greater degree of salinity, but much of data collected show that Station 4 generally gave higher concentrations. This is probably the result of countercurrents.

Conclusions

1—The concentration of the sea water in the Lake Washington Ship Canal is dependent upon (*a*) amount of rainfall, (*b*) number of lockages, (*c*) proper functioning of the salt water drain, and (*d*) methods of disposal of surplus water.

2—If the surplus waters are conducted as much as possible through the lock valves, the degree of salinity can be maintained at a minimum far lower than if the surplus is permitted to run wholly over the spillways.

3—Greater efficiency could undoubtedly be obtained if the salt water basin were enlarged in length and width or depth.

4—Lake Union serves as a secondary salt water basin and prevents the contamination of the water of Lake Washington.

5—Storage of some of the surplus water of the winter and spring months, to be used for drainage through the lock valves during the dry season, would aid materially in decreasing the salinity of the canal system. This could be accomplished by raising the level of the system about one foot.

A Nonstratifying Carbon Disulfide Emulsion[1,2]

By Walter E. Fleming

Bureau of Entomology, U. S. Department of Agriculture, Riverton, N. J.

DILUTE carbon disulfide emulsions are now used extensively to destroy the larvæ of the Japanese beetle, *Popillia japonica* Newm., in the soil about the roots of valuable plants. The concentration of the toxic agent in these emulsions must be carefully controlled in order to obtain the insecticidal action without seriously injuring the plants. It has been the practice, therefore, to prepare the dilute emulsion for such plants by pouring a definite volume of a concentrated (70 per cent) emulsion into the necessary amount of water.

Experience has shown that concentrated carbon disulfide–soap–water emulsions tend on standing to stratify into two or more layers of different carbon disulfide content, which must be agitated again to form homogeneous mixtures. Agitation causes these emulsions to foam and makes their measurement difficult. If the emulsion is not agitated until it becomes homogeneous, the dilution made from the heavier portion will have an excess amount of the toxic agent and is likely to injure the plant, whereas the dilution made from the lighter portion might not kill the insect.

In view of these results, experiments were begun to develop a nonstratifying concentrated carbon disulfide emulsion which could be readily measured in small quantities. The stratifying of the carbon disulfide–water emulsions is caused by the heavier specific gravity and the nonmiscibility of the carbon disulfide. The water of this concentrated emulsion was therefore replaced by certain organic liquids such as benzene, acetone, methanol, and ethyl alcohol, which are miscible with carbon disulfide. Many combinations of these compounds with carbon disulfide and potassium oleate were prepared and tested for their facility of dispersion in water. It was found that a mixture of carbon disulfide, ethyl alcohol, and potassium oleate was the most satisfactory. Further experiments showed that the addition of refined cottonseed oil to the alcoholic carbon disulfide mixture aided the dispersion of the carbon disulfide when the mixture was diluted with water.

In the preparation of a liter of this alcoholic mixture, dissolve an excess of potassium hydroxide in alcohol, filter off the insoluble carbonate, and, after determining the hydroxide content of the filtrate by titration against a standard acid, add sufficient alcohol to obtain a concentration of 13.5 grams of potassium hydroxide per 193 cc. of alcohol. Pour 77 cc. of oleic acid into each 193 cc. of the potassium hydroxide and alcohol solution. Then add 700 cc. of carbon disulfide and 30 cc. of cottonseed oil to each 270 cc. of the oleic acid–alcoholic solution.

The resulting carbon disulfide mixture is amber-colored, transparent, and homogeneous over a relatively long period (at least six months). It is easily measured in small quantities and mixes well with water. It must be diluted initially with an equal volume of water before mixing with the larger quantity of water, used in the insecticidal treatment, in order to obtain a good dispersion of the carbon disulfide.

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[1] Received August 25, 1925.

[2] Contribution No. 1, Japanese Beetle Laboratory, Riverton, N. J.

Academic Research and Industry

Address of James F. Norris, President of the American Chemical Society, at Its Seventieth Meeting, Los Angeles, Calif., August 6, 1925

IN HIS admirable address last year, Dr. Baekeland stated that he had read the addresses of all the past presidents of the SOCIETY. I had not the courage to follow his excellent example. I was afraid I would find that all the words of wisdom had been spoken; that all the valuable ideas had been expressed. I did not want to be hampered by the thought that I was but repeating what had been better said by others. So the problem of this talk was approached in a way not in accord with the scientific method. Ignorant of the literature of presidential addresses, some thoughts were written down boldly with confidence in the good luck that mysteriously looks after the cheerful in spirit.

The attitude taken is consistent with looking ahead rather than behind. The cautious man governs his actions with a knowledge of the past. The statesman acts in the light of history. The reformer does not. The promulgators of revolutionary ideas have been ignorant of the facts or disregarded them. They brought a fresh point of view to affairs. Their very ignorance of what experience had shown to be impossible made the impossible possible. I hope I have caught some of this spirit. At least I have dared to build castles in the air.

These commonplace remarks have been made, not only to excuse myself of ignorance of the wise words of my predecessors, but also as a kind of preamble to an outline of some fascinating dreams that have floated before some of us who have keenly at heart the welfare of our great SOCIETY.

Next year we shall complete the fiftieth year of a continued progress in chemistry since the foundation of the AMERICAN CHEMICAL SOCIETY. We will then stop to hear of great achievements. But today we can look to the future. I once saw a striking play in which two young men were rivals for the hand of the heroine. One was continually prating of his blue blood; his ancestors dated back to Mayflower days and beyond. The other was a nobody of force and character. He finally silenced his rival and won his lady love by saying he had decided that he himself would rather be an ancestor than a descendant.

How can we apply the incident to the AMERICAN CHEMICAL SOCIETY? Fifty years of achievement are about to become a part of the ages. Let us then turn from the past and look to the future. Which path shall we take of those that lie before us? How can the SOCIETY best serve the nation, chemistry, and us who are giving our lives to the science? By making chemistry more vital in the development of civilization and in adding to happiness, comfort, and wealth; by increasing the fundamental knowledge of our building blocks, the atoms, and of the mechanism of their interaction; and by continuing our work of educating the people in regard to what a potent factor chemistry has been and is today in the march of civilization. In the last few years the attitude of the public toward the chemist has changed. He is a man of achievement, a wonder-maker, almost a superman.

How can we take advantage of the great start we have made? Chemistry in America is forging ahead at a rate that startles the world. I have just returned from Europe, where I was one of those who represented America in international gatherings devoted to chemistry. On all sides our achievements are recognized. American chemistry was honored in many ways and always was given the place of distinction. We have only begun our activities and there is much to do before we can finally say we lead the world. When we calmly review the great advances in pure and applied chemistry that have earned the wonder of the world in the last decade, we are chagrined to find that we played no important part in them. We are but followers in the study of the atom; we marvel at the application of known knowledge to the synthesis of compounds of such technical significance as ammonia, acetic acid, and methanol. And we have added only a bit here and there.

Let us see to it that such triumphs are born here in America. I am an enthusiastic internationalist and science is international; but we all have a particular pride which is natural and commendable in the achievements of those close to us. Every father wants his own boy to succeed. It is not provincial, therefore, to want America to take the lead in chemistry.

I again ask the question—what can we do to win the first place and how can our SOCIETY help? The answer to the first part of the question is self-evident, but the way to bring about the result is a problem for serious thought. We must increase the productiveness of research. The past year I have been studying with great care the relationship between chemical research and industrial development. I have visited some of our largest industries based on chemistry and have seen the part played in their development by the work done in their own research laboratories and that produced by the investigators in universities. I was impressed by the fact that the industries are prepared to utilize at once the results of research in what for want of a better name is called pure science. They are supplied with chemists of the best training and of the highest type, who follow eagerly the world's publications. In a paper apparently of theoretical interest is found a fact that the technical man sees he can apply. In one great laboratory I found most of the research men feverishly carrying out work suggested by papers published by two university professors—one in Canada and the other in Germany.

The lesson to be drawn was clear. The work that can be done in the research laboratory of a great chemical organization is of one type—that done in the university laboratory is of another. But both must be done—one springs from the other. Industrial scientific advance has its roots in the academic soil. We are safe in this country to leave the application of chemistry to those who are at present guiding our industries. We of the academic fraternity must see to it that we furnish the acorns from which the mighty oaks will grow.

Relation between Academic Research and Industry

These statements bring me to one of the major subjects of my talk—namely, the relationship between academic research and industrial progress in chemistry. Wherever great progress has been made the importance of this relationship has been recognized. We could well study and follow the example of Germany. It has been my good fortune to see something of the coöperation between the great masters in research and the industrial organizations that have given German applied chemistry such high rank. Let us copy what has proved to be a great success. I am glad to note that such coöperation is increasing in this country. The man who is devoting his life to the study of a particular field of chemistry, who is adding to the world's knowledge by research, and who knows the details of what has been done, cannot help but be of the greatest value to the industry based on his specialty. I have seen and taken part in the industrial development of chemical processes and know that the men directly concerned with the development are aided by the academic investigators, who approach the subject from a more or less detached point of view. I feel confident that our industries will advance more rapidly when they seek more freely such scientific contacts.

The industries can help themselves in another way. They can formulate problems for research of a fundamental character based on their experience. The industrial research laboratories have all they can do to solve their immediate problems. They must deliver a process that works—the dollar mark is the vital symbol in all industrial chemical equations, as our friend Walker puts it. They cannot stop to investigate the very fundamental facts and relationships underlying the processes used. It may take years, and new problems are pressing for solution. We have been cracking petroleum for years, but what do we know of it from the standpoint of real organic chemistry? What do we know of the relationship between lubrication and the chemical composition of the lubricant? Who will solve the chemical problem of vulcanization? A start has been made to get into the hands of the academic investigator fundamental problems which must be solved before many of our industries can pass from the realm of the arts to that of applied science. But much more can be done. Many men in our universities are eager to undertake the study of these problems, but they do not know where to begin or what to study. They do not care to attempt to solve the immediate technical problems: That is the business of the industry itself and should be paid for in dollars.

Although some men of the highest rank look askance at anything of a technical nature, I am sure everyone takes joy in seeing the fruits of his genius and labor become of service to mankind. The ultimate test of value must be usefulness. It may be that the particular orbit of an electron is more specifically defined, but any idea must be capable of being used, to have a value.


Harris & Ewing

James F. Norris

I may be pardoned, I hope, if I say that the Division of Chemistry and Chemical Technology of the National Research Council has for the past few years seen the opportunity of developing our industries in the way I have just outlined. The work is now in excellent order and will be pushed during the coming year. Our great industries have responded cordially and some of the more important fundamental research problems have been formulated. The next thing to do is to win the help of the university men. Steps are now being actively taken to bring about the kind of coöperation which must prove fruitful in time.

A second path is before our university men who wish to devote their energies to the development of our industries. Let them work in those fields of the science which are being applied. We are producers of vast quantities of petroleum products. We have the opportunity to develop great chemical industries based on an abundant raw material. We use this possible source of untold wealth to move from place to place only. Compare what coal tar and petroleum have done to add to our joy in living. Coal tar was studied by the greatest investigators and the results aroused the admiration of the world. I believe petroleum offers the same possibilities. Let American chemists center their attention on the many fascinating problems awaiting solution in this field. By cracking the crude oil we can make hundreds of compounds valuable as sources for myriads of products that will make over our life as coal tar did. I am not suggesting that any one try to make a fortune from petroleum, but that the scientific problems pushing forward for study be approached in the same spirit that led to the triumphs attained in aromatic chemistry.

There are many other fields in which America should lead in pure science. The study of carbohydrate chemistry has just begun. We are making noteworthy progress in the chemistry of the organo-metallic compounds and are taking a commanding position in the study of the application of chemistry in medicine.

I do not mean that university men should become industrialists. Let some of them work in these fields that are being applied so successfully. Everything they do will be recognized and used. The most striking thing in applied science today is the quickness with which the results of academic research are utilized. Twenty-five years passed before any one made use of Faraday's epoch-making discovery of benzene. It would not be so today.

I have said nothing of the kind of research that changes the trend of the investigation of the unknown that lies beyond our present vision. This is logical because I have been speaking of the type of research that is more or less directed. No one would want the whole world to follow on the paths I have indicated. There are always geniuses who go their own way; unfortunately these are but few. We do not attempt to point the road. They should be provided with every material aid, and that is a part of the plan.

I have outlined in a somewhat discursory way how it appears to me chemistry can be made a more vital factor in America. It all goes back to research. The industries should seek more fully the coöperation of individual academic investigators in solving their industrial problems. The industries should point out to the chemical world the fundamental unsolved problems underlying their procedures. Many of our investigators should turn their attention to developing the pure chemistry of the fields upon which our industries are based. The investigator of genius should be encouraged to push his way into the great unknown and should be provided with ample resources for his work.

How Can the Society Help?

How can our Society help to bring all these things about and how can it in perhaps more efficient ways encourage and support research? I said some of us had been dreaming dreams—daytime dreams. We see the fully developed rose in the tiny bud. The bud is the endowment fund, and it lies next to our hearts. I dream of the day when the Society will be supplied with adequate resources to take such a place in aiding research that we shall be the envy of the scientific world. We have just made a start. We must have the coöperation of every member. Each one must feel a personal interest in the success of the effort being made. Each one must see it from an altruistic point of view and at the same time recognize the fact that the development of American chemistry reflects itself on him individually.

The results so far have been encouraging, but much lies before us. Has each man done what his own conscience dictates? Have you been as generous to your science as to your religion?

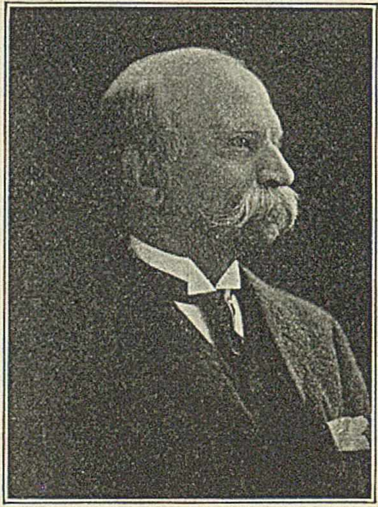
The large sum of money required to foster research as it should be cannot be raised from our own membership. We are not rich but can afford to do a great deal. But after we have done our best another path lies before us. We must go to the public, especially to the men who have amassed wealth as a result of the work of the chemist, and tell them the story of their fortunes. We want to say that our Society to the last member has done its best. We want to tell the banker, the merchant, that his life and happiness have been largely molded by the chemist. We can tell the story of chemistry in a way that many will understand, and I am confident of a favorable outcome. We must, and we shall win.

Don't leave all the delights of achievement to others. Those of us who are steering the ship have an eye fixed on the star. Join the crew and be ready to cheer when we sail into port.

OBITUARY

Charles Frederick Chandler

IT SEEMS as though the youngest of us all were gone—in his eighty-ninth year. His body was old and broken, but his spirit was that of youth to the very end. He was the best of company; his advent was always a joy and an inspiration, for he was one of the most sympathetic of men. The most difficult tasks became easy in his presence. He was a catalyst to encouragement, for he had a remarkable faculty in making men believe in themselves.



C. F. Chandler

As a boy of fourteen he resolved to be a chemist, and he stuck to it. His father, a New Bedford merchant, was addicted to botany and he used to take long walks with him; Louis Agassiz occasionally delivered lectures in his home town, and these he attended diligently. Thus his scientific curiosity was aroused. He also collected minerals, and rigged up a little chemical laboratory. In 1853, at the age of sixteen, he entered Lawrence Scientific School at Harvard. He could not enter Harvard proper and take his work with Professor Jackson, because in his ardor to advance in the physical sciences he had failed to become proficient in Latin and Greek. His opportunity, therefore, lay in attending the Lawrence Scientific School, which was attached to the college but hardly equal in rank, because in those days science did not lead to law or divinity. He continued to work at physics, chemistry, geology, and mineralogy, but the chemistry course was somewhat restricted.

On the advice of Professor Joy of Union, supported by his uncle, Prof. Theophilus Parsons, head of the Law School at Harvard, Prof. Charles T. Jackson of the department of chemistry, and Dr. A. A. Hayes, he resolved to study under Wöhler at Göttingen. He crossed the Atlantic as supercargo on a sailing ship carrying whale oil to Antwerp. He spent about a year at Göttingen working with great intensity under Wöhler, and then under that great man's advice he went to Berlin to work under Heinrich Rose, the father of analytical chemistry. Here he remained nearly a year as private assistant to Rose and taking mineralogy under his brother Gustav. Every week he attended a reception at the house of the American minister, where he met many important persons. He visited Alexander von Humboldt at the Royal Schloss at Charlottenburg, and at Humboldt's cordial invitation remained over two hours in conversation with him. Then he returned to Göttingen for his Ph.D. and came back to New Bedford.

On learning that Professor Joy of Union College needed an assistant he set out post haste to apply for the position. Professor Joy did need an assistant, but he could not persuade the trustees of the fact, and the only appropriation they were willing to make was $400 a year for a janitor.

There never was a man of less false vanity than Professor Chandler. "I'll take the job of janitor," said he, without hesitation, and he proceeded to sweep out, wash up, and do general janitor's work before and after hours, for which he was paid, and to instruct and be the needed assistant in official hours, for which he was not paid. A teacher of geology was wanted and he filled the post; then came mineralogy, which he also taught; and shortly afterwards Professor Joy was called to Columbia and Charles F. Chandler became a professor of chemistry at the age of twenty-one.

In 1864 he was invited to take the chair of chemistry in the Columbia School of Mines, which was opened in November of that year. There was no salary attached to the chair, each professor having to find a living out of the fees paid by students and what he could make outside, so that it was something of a venture. It was not his habit to dicker over terms; he accepted the offer and the school was an immediate success. For many years he was dean of the School of Mines. By 1867 he became professor of chemistry at the College of Physicians and Surgeons, and for a long time, until its merger with Columbia University, he lectured four afternoons a week to the medical students.

The New York College of Pharmacy had one room in the old New York University Building on Washington Square, and twenty-three students. They had no money but they had great need of instruction in chemistry. So Professor Chandler gave them three evenings a week for five months, gratis, and then they allowed him $400 a year for an assistant and chemical apparatus. Finally, the college grew to be a big establishment with its own building on 67th Street, and Dr. Chandler was made president until it too was absorbed by the great university.

The Metropolitan Board of Health of New York was composed first of aldermen and later of physicians, and the physicians needed chemical advice. But they had no funds to pay for such services. The occupant of three chairs of chemistry, however, didn't mind that; he always had time to give to any worthy cause, and being asked to work for nothing he straightway complied. He first took up Croton water, which was getting the blame for all sorts of diseases that could not otherwise be explained. He found it to be of prime quality, that no better water was furnished to any city. Then he examined the milk supply, and after long and bitter political struggle he established proper guaranties of pure product. Kerosene lamp explosions were frequent; the first year he took up his work in this department fifty-two persons, mostly women and children, were burned to death from this cause. He established, again after a battle royal, the present standards of illuminating oils. In 1873 he was appointed president of the Board of Health and for ten years he held the office. He stopped the building of unsanitary tenements and put through the first tenement house legislation. Sewer gas was a bugaboo among physicians and he proved this to be an illusion, but he set about to improve plumbing, which was very defective. He designed the method still in vogue for keeping water seals tight, and he proposed the now universally used flush closet.

There are two orders of Great Chemists: the Dynamic Forces and the Lucky Strikers. Professor Chandler constantly attributed his achievements to his great luck, but that was sheer modesty. We cannot review his life without immediately perceiving that about the only real luck he had was in marrying. It was his own dynamic force and his extraordinary vision that constituted the key to his great achievements.

He made leading contributions to the sulfuric acid industry and to the distillation, standardization, and use of petroleum. He discovered and passed on the ingenious system of ton-weight assaying, which is a boon to the metal and metallurgical industries. He was the father of modern sanitation. Indeed, his contributions are so many and so various that one is in danger of "missing the trees for the woods."

He would take all sorts of chances against himself, but he was adamant against running risks for others. His generosity was unbounded. His students were always his first concern. At times his income was high, but much of it went to help students who otherwise could not have continued their studies. If his liberality was abused he straightway forgot all about it.

Still another tax on his fortune was the Chandler Chemical Museum at Columbia. For nearly half a century he collected materials for this great assembly of chemicals and chemical products. Whenever he saw a product of chemical industry that was rare or of precious beauty, he could not resist the temptation to buy it to enrich the museum and "to show my boys."

His boys were his constant delight and his ever-present care. He knew how, as few others who have lived, to open the portals of chemistry to a pleasing and attractive vista. He aroused curiosity and ardor. He was a mighty force in the introduction of chemistry into medicine. Wherever we go we find traces of this remarkable man—in industry, in sanitation, in the household, and in the improvement and comfort and safety of living. He was a gentleman to his finger tips, who never forgot his own obligations. His friendship was a benediction.

Ellwood Hendrick

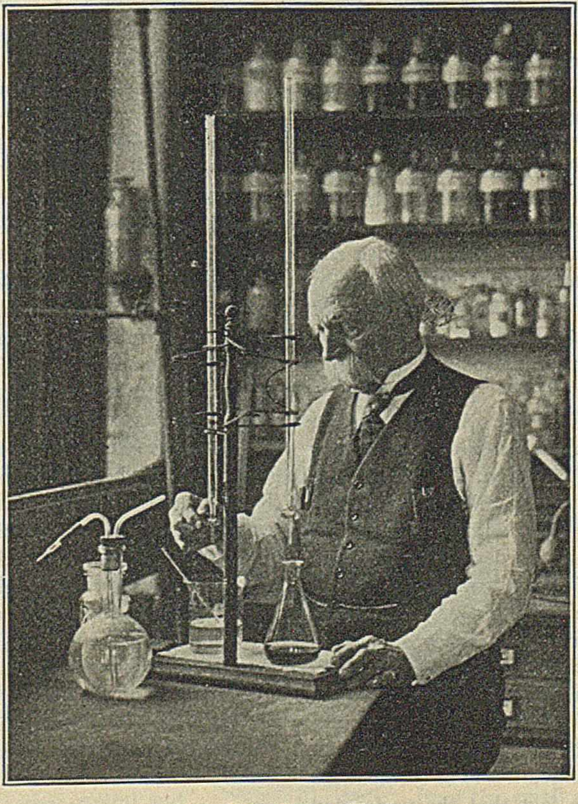
Biographical

Charles Frederick Chandler was born at Lancaster, Mass., December 6, 1836, and died at East Hartford, Conn., August 25, 1925. He began his education at the New Bedford High School, and took his advanced work at Harvard and Berlin. Göttingen conferred its Ph.D. upon him in 1856, and he was given the honorary M.D. at New York University in 1873, honorary LL.D. at Union College in 1873, honorary Sc.D. at Oxford in 1900, and honorary LL.D. at Columbia University in 1911. Among his many other honors may be mentioned his presidency of the American Chemical Society in 1881 and again in 1889. He was also president of the New York Chemists' Club in 1899 and of the Society of Chemical Industry in 1900. In 1919 the New York Section of the Society of Chemical Industry bestowed upon him its Perkin Medal.

Dr. Chandler was one of the founders of the American Chemical Society, if indeed not the individual most responsible for the formation of the Society. On January 22, 1876, a circular was issued inviting those interested to meet for the formation of a chemical society, and Dr. Chandler was the first to sign this communication. It was at first intended to form a local chemical society in New York, but such wide interest was evidenced that on March 22, 1876, a further letter indicated that a national society would be formed. At the organization meeting April 6, 1876, Dr. Chandler presided, and although he declined to become the first president on the ground that the honor should go to an older and better known man, he did become vice president. The early records show that he was the active official of the new organization. In 1870, with his brother, W. H. Chandler, he founded the *American Chemist*, of which he was editor and part owner. After six volumes the publication was abandoned in favor of the *Proceedings of the American Chemical Society*, which two years later became the *Journal of the American Chemical Society*.

Dr. Chandler was assistant in chemistry at Union College in 1857 and professor from 1857 to 1864. He taught analytical and applied chemistry at the School of Mines, Columbia University, from 1864 to 1877, and was adjunct professor of chemistry and medical jurisprudence at the College of Physicians and Surgeons from 1872 to 1876, and professor there from 1876 to 1897. He taught chemistry at Columbia University from 1877 to 1911, after which time he held the title of emeritus professor. Dr. Chandler also served as professor of organic chemistry and president of the New York College of Pharmacy, and as chemist and later as president of the Metropolitan Board of Health of New York City. Among his last activities were those as consulting chemist of the Chemical Foundation, Inc.

In 1909 he was a delegate to the International Congress of Applied Chemistry in London. He was an honorary member of the American Chemical Society, a member of the National Academy of Sciences, the American Association for the Advancement of Science, the Society of Chemical Industry, the American Institute of Electrical Engineers, the American Institute of Mining and Metallurgical Engineers, the Philosophical Society, the New York Chemists' Club, the New York Academy, the London Chemical Society, the Chemische Gesellschaft, and the Société Chimique de Paris.



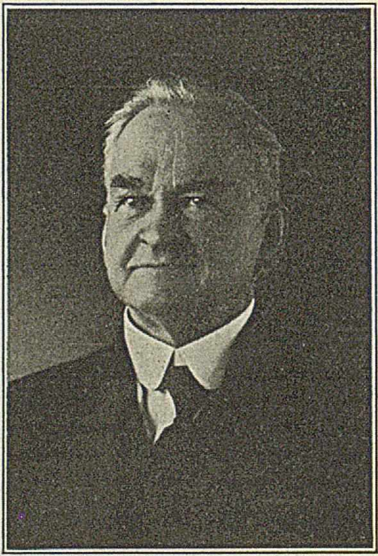
Dr. Chandler at Work

AMERICAN CONTEMPORARIES

Frederick Noah Pease

MR. PEASE is a recognized pioneer and authority on chemistry applied to transportation, or, as better stated by President Hadley of Yale University, "a leader in making chemistry a handmaid in the service of the people." He entered the service of the Pennsylvania Railroad Company as assistant chemist in 1881, succeeded the late Charles B. Dudley as chief chemist in 1912, and on reaching the allotted age of threescore years and ten was retired on January 1, 1921, this being his personal wish.

It is not the purpose in this short space to review his scientific work and publications. These attainments are referred to in *The Yale Alumni Weekly* of July, 1917, and "The Life and Life-Work of Charles B. Dudley," published by The American Society for Testing Materials. The former reference is in connection with the honorary degree of master of arts conferred upon him by Yale University, and the latter gives a list of his joint publications. We prefer to be more personal and to describe those traits which may give encouragement to others, especially to those of the coming generation who have not as yet found their life's work. In passing, however, it is to be remarked that the foregoing references do not bring out his ability as an analyst. He studied Fresenius before he went to college, and during his professional career he studied the analytical methods published in the technical journals in English, French, and German, many of which were put to the actual test as to accuracy, and in some cases they were improved in his hands. For example, in the method for the determination of phosphorus in steel, based on the precipitation of the phosphorus as phosphomolybdate, and its subsequent estimation volumetrically by reduction with zinc and titration with potassium permanganate, he found that by proper technic the resulting reactions were to Mo_2O_3 on reduction and to MoO_3 on oxidation. Earlier investigators had based the equation on the reduction from a complicated oxide, some using the factors $Mo_{12}O_{19}$ and $Mo_{24}O_{37}$.



Frederick Noah Pease

Mr. Pease was born on December 3, 1850. At the early age of four he was left an orphan, whereupon his grandparents took him to their home in the village of Ellington, Conn. At this period of his life he was not robust. He had little opportunity to play with other children of his own age, and therefore relied much on that form of amusement which he devised for himself. In his early boyhood he accidentally found a worn volume of an old edition of "The Elements of Chemistry," by J. L. Comstock. In this book he became intensely interested, and it was his close companion. He put into practice many of the experiments suggested, and verified to his own satisfaction the statements of the author. Among the experiments which he made might be mentioned the preparation of hydrogen with the appliances which he was able to assemble. The difficulties to be surmounted in this endeavor are indicated by the fact that the perforated stopper which he used was made by his hands from a wood block. Acid and zinc were obtained from the village druggist. He also made charcoal by heating wood for several hours in an extemporized crucible imbedded in the coals of the living-room heater. An accident made this experiment memorable, the hot charcoal having been accidentally spilled on the oilcloth of the living-room. One of his most ingenious experiments consisted in making oil gas and applying it. A discarded gun barrel served as his retort, the source of heat was the living-room fire, and a gasometer was constructed from such utensils as he could find. A homemade burner enabled him to illuminate a room in his grandfather's home with the gas which had been prepared and collected.

In conjunction with the book that had become his friend, he became interested in the popular science references given in the family magazine, which was devoted principally to politics, literature, science, and arts. He always looked forward to the arrival of this magazine, and was keenly disappointed when the science section was neglected by the editor. We refer to this as a conspicuous illustration of the value of a popular science section in the magazines and weeklies of the day, as they very frequently aid young boys in finding their work for life.

It will readily be appreciated that the experiments conducted in the village home at Ellington became known to the neighbors, and the young investigator acquired early local notoriety. His work came to the notice of Professor Lyman of Yale University, who persuaded him to prepare for entrance to the freshman class of Sheffield Scientific School. Mr. Pease accordingly prepared for college at the Edward Hall Preparatory School of Ellington and entered Sheffield Scientific School in 1871, from which he was graduated in 1875. His work at college drew his instructors and professors to him, many of whom remained his loyal friends through life.

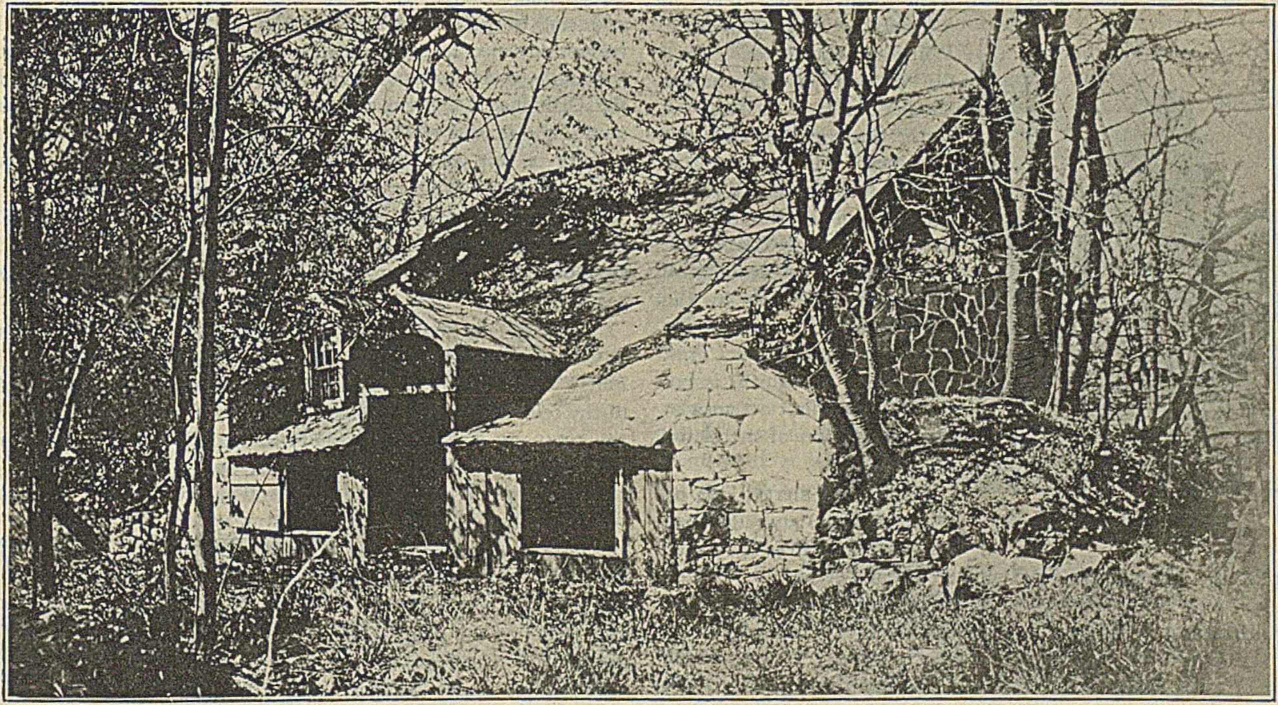
Since his retirement from active service as chief chemist of the Pennsylvania Railroad System, he has continued to pursue his laboratory studies in his home, with special reference to radiophony. He has constructed numerous receiving sets, illustrating different accepted principles, and he is now working on a new one which it is hoped will result in an improvement in selectivity. Regardless of the merit of what he may achieve in this work, the world will not hear of it unless advised by a mutual friend. He is also interested in the scientific studies of other investigators who are endeavoring definitely to disclose the structure of the atom. Philosophy has always appealed to him.

It is still a delight to visit him and listen to his discussion of the higher things of life which have been the theme of the true philosophers of the past. One can obtain a slight conception of this pleasure by studying his expression in the accompanying picture taken on the occasion of his retirement on January 1, 1921.

M. E. McDONNELL

AMERICAN CHEMICAL INDUSTRIES

E. I. du Pont de Nemours and Company



Oldest Powder Mill in America. Built by E. I. du Pont in 1802, Wilmington, Del.

THERE are a number of interesting facts not generally known to chemists or the people in general of this generation, which had a bearing on the foundation in 1802 by Eleuthere Irenee du Pont de Nemours of what today has become one of the largest and most constructive chemical manufacturing corporations in this country, if not in the world.

His father, Pierre Samuel du Pont de Nemours, though educated for the practice of medicine, devoted himself to literature and politics. He took a prominent part as a "Moderate" during the French Revolution and showed indomitable courage in his efforts to save his country. He and his son suffered imprisonment with his friend Lavoisier and only escaped the guillotine through the timely death of Robespierre. He was a friend of such men as Benjamin Franklin, Lafayette, Talleyrand, Turgot, and Quesnay. He and his son both fought in defense of the King on the memorable tenth of August and besides being president of the Constituent Assembly, he held other important offices.

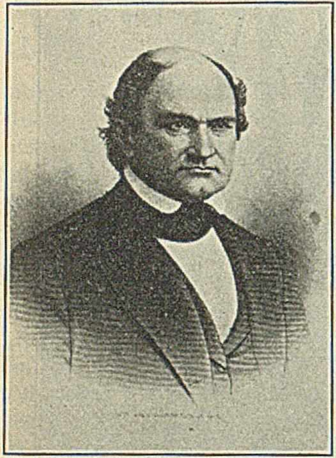
In 1788 as a boy of sixteen, E. I. du Pont began the study of chemistry at Essonne in the laboratory of Lavoisier, who was at that time in charge of the manufacture of gunpowder for the French Government. It was here that young du Pont became familiar with the manufacture of gunpowder. Lavoisier's position was one of the first to be suppressed by the revolution in 1791, and du Pont joined his father in the publishing business. In 1799, owing to broken fortune and the unsettled conditions in France, the entire family came to this country, father and son having raised capital and formed a company for the purpose of developing unused land in the South. While out for a day's shooting with a friend they had shot away all of their powder and bought a new supply in the neighborhood. The high price and bad quality of the powder led him to investigate the industry in this country and then he became convinced that there was real opportunity for a powder factory to be built and managed along the lines of the French Government works.

He immediately returned to France and raised by subscription among his friends some $36,000 and ordered the necessary machinery and raw materials to start his enterprise. His machinery was made at the Arsenal and Government works at Essonne and his plans were made by French Government draftsmen. In a letter to his father six years later he wrote: "In four years I have made 600,000 lbs. of powder that would have come from England if I had not made it; therefore it is only the English I have injured. This truth was well understood in France when I was given every facility for procuring my machinery." So it was that this young chemist, or rather chemical engineer, founded the business which has developed into the great du Pont institution of today.

E. I. du Pont died on October 31, 1834. He was a man of great courage and of indomitable will to overcome great, and at times what appeared to be insuperable, difficulties, of sterling integrity and a lovable character worthy of his great father. These characteristics have been dominant in all of his descendants who have had the privilege of carrying on the great business which has been developed from the small one that he founded.

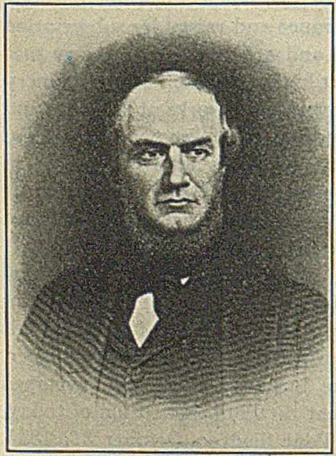
In the early days the company sold refined saltpeter, charcoal, pyroligneous acid, iron liquor (a red dye), and creosote—a very considerable line of chemicals.

E. I. du Pont's son, Alfred Victor, succeeded him in the management of the business. He studied chemistry under Thomas Cooper in Dickinson College who taught science there from 1811 to 1815 and afterward in Philadelphia. Cooper was a thorough scientific investigator and, judging from young du Pont's own work, he was undoubtedly inspired and trained to carry out his researches in a truly scientific manner. While at Dickinson, Alfred du Pont made a study under Cooper of the colors imparted to the flame by metallic salt solutions. The procedure consisted in dipping a bit of cotton in a solution of some chloride, pressing the cotton, then dipping into alcohol and holding the cotton in the flame of a lamp, to which the color was imparted. This, says Edgar F. Smith, is undoubtedly a first attempt at the recognition of metals by colored flames.


Alfred du Pont
President, 1834 to 1850

He was ever alert to keep up with his times and, although England and France refused to purchase Schoenbein's patents on "Gun Cotton" or "Cotton Gunpowder," he determined to investigate it himself. He wrote: "The discovery is brilliant and such as to create astonishment, but the introduction of gun cotton in common use must be the work of time because the cost of preparing it is high and it will require years before the application of machinery to its manufacture can make it cheap enough."

His experiments on gun cotton which he made himself led him to the above conclusion. His conclusions have proved correct, as it was thirty to forty years before this material became useful for either military or commercial purposes. Alfred du Pont devised a new instrument, with which he proved the interesting fact that there is no relation between the strength and the quickness of gunpowder. He also considerably improved the manufacture of sporting powder.


Henry du Pont
President, 1850 to 1889

In 1850 Alfred resigned and the management fell upon his brother Henry, who was educated at West Point and served for some time in the Army. Henry du Pont was not a chemist, but his engineering training gave him an interest in efficiency and reduction in cost of manufacture. His partners were his brother Alexis and his nephews E. I. du Pont, 2nd, and Lammot. Irenee du Pont, 2nd, after much experimentation introduced and patented the metal keg, which has been used now for many years for packing black powder.

From the very beginning the business was conducted as a partnership and was entirely managed by the senior partner, and in 1899, when the business was incorporated, all the stockholders were members of the family. The younger members of the family were factory superintendents and in general became partners after years of experience or when a reorganization took place owing to the death or retirement of a senior partner.

Lammot du Pont, son of Alfred Victor, was referred to in 1853 as "our chemist," four years after his graduation from the University of Pennsylvania. In 1857 he introduced the use of nitrate of soda in place of nitrate of potash in the manufacture of blasting powder, for which he secured a patent. This discovery was a very important one, not only financially but as an advance in the art. He was a chemical engineer of great ability and not only built a new powder factory in the anthracite region but also later built what has since become the largest dynamite plant in the world. He developed new powders for the Ordnance Department and was a pioneer in the development, of not only black prismatic, but also of brown prismatic powder in this country. Some of this development took place before the Civil War.

Owing to scarcity of saltpeter its production from Chile saltpeter and potash was started in several places by double decomposition, and this process has been carried on by the company ever since.

Mrs. B. G. du Pont, in her history of E. I. du Pont de Nemours & Company, from which much of this material is taken, says of him: "The chemical work in which he was so successful kept him in the refinery and in the laboratory very constantly." In 1872 the company was making twenty-four kinds of gunpowder and seventeen kinds of blasting powder, and sold as by-products refined saltpeter, sulfur, charcoal, and safety fuse.


Eugene du Pont
President, 1889 to 1902

Alfred Nobel's patent for the process of making nitroglycerol in 1865 soon came to the attention of the du Ponts, but owing to the many accidents that occurred in its manufacture Henry du Pont, then head of the firm, would have nothing to do with it; in fact, when Nobel's own plant near Stockholm blew up in 1869, its importation into England and Belgium was prohibited. It was not until 1876 that he admitted that Hercules powder (black powder soaked in nitroglycerol) was the best of all explosives.

Lammot du Pont, however, was not satisfied and the records show that he had been experimenting on the new explosives, for he felt that the day must come when his firm would do its share of the manufacture. He made plans for a dynamite plant, and in January, 1880, it was announced that the company was going into the manufacture of high explosives. He organized the Repauno Chemical Company and became its president, resigning from the parent company in January, 1882. He not only designed the plant but laid out the details of the experimental work. He was brilliantly successful and founded also a great industry. Unfortunately, in carrying out some plant-scale experiments on the separation of nitroglycerol from the waste acid to save the latter, instead of drowning it all in water as had been the practice, he was killed by an explosion, and his brilliant career was brought to an untimely end. Mrs. du Pont in her book says: "Lammot du Pont's death was an appalling loss to the firm. He was a brilliant chemist, a skilful and practical machinist, fearless almost to recklessness in experimenting, etc."

Eugene du Pont, who became head of the firm in 1889 and first president of the corporation in the same year, was educated at the University of Pennsylvania. He spent much of his life in factory management and in the laboratory in the development of brown prismatic powder, assisted during part of the time by Francis G. du Pont. In 1884 the du Pont Company succeeded in making brown prismatic powder which was satisfactory to the Government, and in 1889 a thorough investigation of European powders of the same nature showed that they were not superior to the du Pont powder. This work involved a long research in the preparation of a proper form of charcoal. Much of the important mechanical work in devising safe, efficient presses for the production of this powder was done by Alfred I. du Pont.

Francis G. du Pont was educated at the University of Pennsylvania and afterwards studied chemistry under Professor Genth and became an efficient chemical engineer. He not only superintended the manufacture of powder at home, but designed and built the Moor plant in Iowa and made all the drawings and blueprints in his own home. He was the inventor of, and developed the manufacture of, the celebrated du Pont smokeless powder, and with the assistance of Pierre S. du Pont, afterwards president and now chairman of the board of the company, and also with Francis I. and other members of the family, developed the manufacture of government military smokeless powder. Francis I. du Pont studied chemistry at Yale.

Pierre S. du Pont and Irenee du Pont, now president of the corporation, are chemical engineers from the Massachusetts Institute of Technology, and Lammot du Pont, first vice president, is a civil engineer from the same institution.

Up to the time of the death of Eugene du Pont in 1902, practically all the partners and superintendents of the works and stockholders of the original firm and corporation were members of the family, extending over a period of one hundred years. At that time none of the older members of the company were willing to undertake the management either on account of ill health or for other reasons. The affairs and interests of the company had become so complex that it was decided by the majority of the stockholders to sell out, so Alfred I. du Pont in conjunction with a cousin, T. Coleman du Pont, now Senator du Pont, and the above-mentioned Pierre S. du Pont, organized the E. I. du Pont de Nemours Powder Company, which bought out the old company and consolidated all of the interests of the old company into the new one.

This move brought about a new era in the history of the company—all of the black powder, dynamite, and smokeless powder interests being brought together. Just before this consolidation the Eastern Dynamite Company, which controlled the Repauno Chemical Company and other dynamite companies, established the Eastern Laboratory for research and soon afterwards the company organized another research laboratory called the Experimental Station on the Brandywine. In 1911 these two laboratories were placed under a common head as chemical director of the company.

With the manufacture of dynamite and smokeless powder, the manufacture of nitric acid and sulfuric acid, ammonium nitrate and acid recovery became necessary with the accompanying employment of many chemists. Among the older chemists connected with the dynamite end of the business should be mentioned John C. Schroeder, R. S. Penniman, many years superintendent of the Kenvil plant, and O. R. Jackson, superintendent of the Repauno plant after the death of Lammot du Pont.

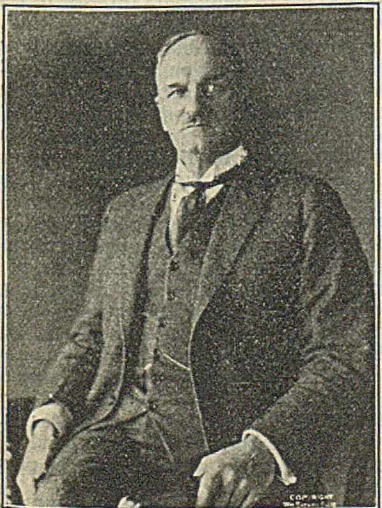
From 1902 to 1912 the business was very successful, but during the latter year part of its business was separated from it by decree of the United States Court and two independent competing companies, the Hercules Powder Company and the Atlas Powder Company, were created out of its substance. The court was so convinced that much of the du Pont Company's success was due to its research laboratories that it required the laboratories of the du Pont Company to serve the two new companies for a period of five years. The court was afraid that new developments in these laboratories might prevent the success of the new companies.

After this dissolution it became necessary for the company to find new useful fields for its expanding financial resources, and it decided to embark into chemical lines other than explosives, but related to the chemical activities with which it had had experience. It purchased the paint and heavy chemical business of Harrison Brothers & Company, which was founded in 1793 and has an interesting history in itself. Based on the use of cellulose and nitrocellulose, it embarked on the artificial leather business, the pyralin, the pyroxylin lacquer, the artificial silk or Rayon, and the Cellophane business, and only recently has decided to enter the synthetic atmospheric nitrogen business.

The entry into the dye business was logical owing to its close relation to the explosives business, and particularly to those processes involving nitration reduction, etc., such as trinitrotoluene, picric acid, and tetryl.

The company's development and activities during the World War are too well known to require attention at this time, but it is interesting to note that a company founded by a French powdermaker more than a century and a quarter ago was in a position to be such an important factor in saving the French Republic from defeat with ample supplies of powder.

Charles L. Reese



Wm. Shewell Ellis, Wilmington, Del.

Left—T. C. du Pont,
President, 1902 to 1915
Right—Pierre S. du Pont,
President, 1915 to 1919
Upper—Irenee du Pont,
President, 1919 —

BOOK REVIEWS

Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists. Compiled by the Committee on Editing Methods of Analysis, R. E. Doolittle, Chairman. 2nd edition, revised to July 1, 1924. xvi + 535 pages. Published by the Association of Official Agricultural Chemists, Washington, D. C., 1925. Price, $5.00.

The present volume is an expansion of the 1920 edition, which contained methods revised to November 1, 1919. The book has undergone a notable expansion, it being approximately 25 per cent larger in the descriptive matter and tabulated appendixes. Two new chapters have been added—one on liming materials and one on gelatin. Methods for sugar products have been combined into a single chapter and those for brines and salts added to the chapter on water. The result is a volume giving a large number of analytical methods which are applicable not only to the problems of the agricultural chemist, but in many instances equally adaptable to other forms of chemical analysis. To take exception to any portion of a work of this character savors of the meticulous, and yet as one examines the book from the standpoint of the potential user, certain points present themselves upon which comment reasonably may be made. For example, in the first chapter three methods are given for determining total nitrogen with exclusion of the nitrates—namely, the Kjeldahl, the Gunning modification, and the so-called Kjeldahl-Gunning-Arnold method. All of these are indicated as official, and so presumably equal weight is given to them all. The only difference between the two latter lies in the relative amounts of the sulfates used. From the practical standpoint it would seem advisable to indicate one of these methods as being most satisfactory, and, if desired to include the others, merely to indicate them by reference.

In the standardization of hydrochloric acid, one wonders why the chloride method as developed at Harvard in connection with the atomic weight work there is not given a place. Eliminating the time-consuming use of the nephelometer, the method still gives results which are both highly sensitive and accurate, even in the hands of the relatively inexperienced.

In the standardization of sulfuric acid the writer would question if the ignition of the barium sulfate and filter paper does not introduce the possible danger of a slight reduction of the sulfate to sulfide. Moistening with a drop of sulfuric acid and again igniting eliminates this possibility.

A third question concerns the procedure of neutralizing the acid mixture prior to distillation. The strong caustic soda solution is poured down the side of the flask to avoid mixing, and then the flask is connected with the condenser. There is the possibility here of a loss of ammonia—small, it is true, but still significant—from the point where the alkali enters the acid mixture. A safer practice lies in the use of an inlet tube reaching to the bottom of the flask, and through this the alkali can be poured after assembling without the danger of ammonia loss.

Without going too much into detail, some criticisms may be raised of the determination of arsenic in the chapter on Metals in Foods. The substitution of mossy for the stick zinc, the use of apparatus closed with ground-glass joints rather than with rubber stoppers, and the standardization of the moisture content of the lead acetate cotton are all points worthy of consideration. The admirable series of papers by Sanger and his associates gives details of much value in this analytical procedure.

To take but one more point. The description of the Hortvet cryoscope would gain in clarity if a diagrammatic sketch of the apparatus were used rather than the advertising cut. In the computation of the corrected freezing point lowering as determined by this instrument (page 267) it is not quite clear why the depression produced by 7 grams of sucrose is assumed to be correct at −0.420 degrees when above this on the same page the freezing point is given for this solution as −0.422. If an interval correction is to be applied, it would seem to be as necessary to correct the larger initial segment as the smaller interval between the freezing point of the sucrose solution and that of the milk.

As stated initially, to offer adverse criticisms on such minor matters would be highly questionable were it not for the fact that this compilation bears an official stamp, and is offered to the public as the tried and proved best of available methods. In the main, the volume amply bears out this implication and adds a most valuable instrument to the equipment of the analytical chemist. The chemical world at large is under a heavy debt of obligation to the association, its editing committee, and the large number of experts who have participated in the compilation of this most excellent manual.

Allan Winter Rowe

Management's Handbook. By a Staff of Specialists. L. P. Alford, Editor-in-chief. 1607 pages. The Ronald Press Co., New York, 1924. Price, $7.50.

For the first time the science of management is given a well-formulated, concise, and thorough handbook. The completeness of this book would indicate that the science were many times older than the short quarter of a century which has seen this development in industry and business come into effective coöperation.

The field of usefulness of this book embraces the entire range from the student of management to the biggest executive. It should prove useful to those responsible for policy, production, marketing, financial operation, and all inter-related activities in the great realm of industry.

The list of sections is in itself an excellent recommendation to officials having charge of management matters. It is of increased significance, however, when considered in conjunction with the names of the editor-in-chief and editors of the various sections, which constitute an enviable "Who's Who in Management," and insure the most complete and authoritative information.

As a matter of record, Verein Deutscher Ingenieure, one of the leading engineering societies of Germany, has secured permission to translate Management's Handbook into German, because it is recognized that it will be of tremendous help in advancing the development of German industry. Such an arrangement is indeed an outstanding compliment to American management, and especially to the editors of this book.

A. C. Oliphant

Organic Derivations of Antimony. By Walter G. Christiansen. American Chemical Society Monograph. 230 pages. The Chemical Catalog Co., Inc., New York, 1925. Price, $3.00.

This volume has for its object the correlation of widely scattered data presented in numerous papers dealing with organic antimonials in such a way that the information may be available "both for those desiring a general knowledge of the organic derivatives of antimony and for those embarking on research in this field." This has been accomplished by the author in a singularly fortunate way. Even an organic chemist familiar in a general way with the chemistry of these compounds cannot fail to be surprised at the diversity of methods which have been developed, especially within the past few years, for the preparation and interconversion of various types of antimonials.

The special stimulus which led to expansion in this field seems to have been a suggestion made by Mesnil and Nicolle in 1906, that antimony derivatives might be of use in the treatment of trypanosomiasis. This proposal led to immediate interest in the preparation of new antimonials and probably stimulated indirectly the investigations which resulted in the discoveries made and patented by the Chemische Fabrik von Heyden as early as 1912. But the exact nature of these discoveries was not known until the publication of a series of articles by Schmidt commenced in 1920.

The present monograph was published in connection with the study of antimonials now being made by the Departments of Pharmacology and of Tropical Medicine at the Harvard Medical School.

Chapter 6, Antimonials as Therapeutic Agents, contributed by George C. Shattuck, M.D., presents an interesting survey of the value and treatment of certain tropical diseases. The success which has accompanied the use of antimonials in the treatment of Leishmanioses, and especially their effect upon three varieties of Schistosoma, furnishes conclusive evidence of the great possibilities which the study of antimonials as therapeutic agents offers. In the case of these three varieties of Schistosoma, arsenicals have failed to prove useful, while antimonials are regarded as specific for the diseases. Even the ulcerative lesions of leprosy seem to have yielded to treatment with antimonials.

The author is to be congratulated on the very satisfactory presentation of his subject matter.

Lauder W. Jones

Bibliography of Bibliographies on Chemistry and Chemical Technology, 1900-1924. *Bulletin of the National Research Council* 50. Compiled by C. J. West and D. D. Berolzheimer. 308 pages. Price, $2.50.

With the present available supply of chemical literature so extensive and scattered, which makes it more and more difficult to make a complete search even in one specialized field, a good bibliography is always welcomed as an invaluable time-saver. Many such bibliographies covering various fields of the chemical science do exist. However, these too are widely scattered, like the original references from which they are compiled, and require many hours of tedious and painstaking work to locate them all. To compile these scattered bibliographies into an easily usable reference book, with descriptive material to make them more valuable, has been the task which the authors of this book have accomplished to an admirably successful degree, giving to the chemical profession and to the scientific world as a whole a contribution which will mean hours of time saved.

This Bibliography of Bibliographies on Chemistry and Chemical Technology is the third of a series of collective bibliographies the preparation of which has been undertaken by the Research Council; *Bulletins* 36 and 47, being similar works in the fields of Geology, by E. B. Mathews, and of Physics, by K. K. Darrow, respectively.

The book under review is divided into five parts, as follows: Part I—General Bibliographies, Part II—Abstract Journals and Yearbooks, Part III—General Indexes of Serials, Part IV—Bibliographies on Special Subjects (main section covering 294 pages), and Part V—Personal Bibliographies.

The typography throughout the book is fine. The standard abbreviations of *Chemical Abstracts* have been used throughout.

It seems safe to predict that this book will prove a most valuable asset to all its users, and members of the chemical profession and librarians alike will feel that the authors have rendered them a valuable service in publishing this compilation.

Arthur R. Cade

Chemistry in Modern Life. By Svante August Arrhenius. Translated from the Swedish and revised by Clifford S. Leonard. Library of Modern Sciences. 286 pages. 20 illustrations. D. Van Nostrand Co., New York, 1925. Price, $3.00.

It is well to have among us a philosopher such as Svante Arrhenius to point out that chemistry and its gifts to society are only part of the great moving panorama of life and that at present our contribution to modern civilization is dependent largely on highly concentrated crude products which, as we utilize them, revert to so dissipated a form that they become useless for a further cycle—that is to say that inevitably we are using up and destroying forever the materials out of which we make so many valuable products. Not only that, but we are using very rapidly those products which enable us to harness energy by chemical change—coal and oil. In his book Professor Arrhenius reviews the outlook, not alone as it is now, but as it may be in a very few years as contrasted with the whole span of human existence; and he concludes that we must practice rigid economy until such time as our research shall have placed us in a position of independence regarding the crude materials of those numerous industries which we call chemical.

In his treatment of the subject the author breaks away from the traditional method of making brief statements of the most sensational facts growing out of our use of chemistry. He wishes his reader to understand the methods of the chemist as well as his achievements, and therefore he outlines, to begin with, the theoretical and experimental basis upon which the science rests. This outline is remarkably lucid and very concise. It should serve as a model for those who wish to make a complicated subject intelligible in a brief description. Having brought his reader into contact with the fundamental theories of the science, he next reviews the part that chemistry has played in giving us those aids which mean so much to our civilization: our advance in controlling oxidation, in fashioning new tools of materials which are better than those our forefathers had at their disposal, in passing from the crude clay pot to the triumphs of the structural engineer having at his disposal cement. The chemistry of the earth's crust is then described and we are taught the proper courses of action to conserve and utilize what is our heritage.

Professor Arrhenius does not hesitate to employ terms which must be foreign to the vocabulary of most men and women, even though they are well read in the sciences, and in Chapters X and XI he even describes electrolysis and chemical equilibrium in no simple terms. From these he runs to a more descriptive treatment of certain fields—dyes, perfumes, drugs, cellulose, and rubber—concluding with the question of the food supplies of peoples and the conservation of the resources that Nature has given us.

The reviewer doubts that the average layman will be able to read the book, except the first chapters and the last. Moreover, it is a question whether it is really an advantage to give such minute detail in a treatment of this kind. The author has an enormous range of facts at his disposal because of his very profound knowledge, and occasionally he crowds too many of these facts into a few sentences. They hammer on the reader's attention and produce a stupifying effect; moreover, they tend to slow down the story. However, for the teacher who wants to find facts the book should prove extremely useful.

Dr. Leonard has made a good translation, but he has allowed certain mannerisms to creep in, as the translator frequently does, and this results in the use of un-English words and expressions. Also there are far too many typographical errors, some of them giving a false meaning to the statements made.

It is good that this book has appeared, because it emphasizes a side that is of the utmost importance to everyone who has the welfare of chemistry, as a part of the well-being of humanity, really at heart.

R. E. Rose

The Chemistry of Wheat Flour. By C. H. Bailey. American Chemical Society Monograph. 314 pages. The Chemical Catalog Co., New York, 1925. Price, $4.00.

The announcement of the inclusion of a monograph on the Chemistry of Wheat Flour by Dr. C. H. Bailey in the A. C. S. Monograph Series received general approbation from all those interested in the field of cereal chemistry. Dr. Bailey's years of experience in this field and his many important contributions to our knowledge gave assurance that the work would be comprehensive and adequately evaluate our present information, and also point out the gaps and need for further study.

The appearance of this volume has fully justified all these expectations. The author is to be congratulated on the accurate, logical development of his subject, the constant evidence of a very careful survey of the available literature, and the readable and flowing manner in which the various chapters are presented.

In the introduction the author states: "Properties of flour must be considered in their relation to: (1) the raw material from which it is manufactured, or wheat; (2) the process of manufacture, or milling; (3) its adaptability to the principal use to which the flour is put, or baking." This plan has been followed closely. The first six chapters of approximately one hundred pages are devoted to a consideration of wheat, the raw material. At first glance the reader is inclined to feel that the chemistry of the wheat plant, influence of its environment, etc., are unduly stressed. However, the author has anticipated this comment, and justifies the space accorded these phases by stating: "It was deemed advisable to consider these phases of the subject at some length because of the fact that roller milling is essentially a mechanical process, and the flour miller cannot incorporate anything in the flour (aside from bleaching agents and flour improvers) which is not found in the wheat. Hence, the influence of any factor affecting the properties of wheat becomes of immediate interest to the miller and baker since these influences may be reflected in the properties of flour milled from the wheat."

The volume is remarkably free from typographical errors, and the illustrations are clear, as well as the many tables which appear throughout the volume.

The reader's understanding of a number of the tables would have been easier had some explanation been given of the use of numbers applied to color and crumb score, as well as gasoline color value. The numerous analytical determinations given in the various tables or context on the moisture content, ether extract, etc., do not always indicate the methods followed by the authors whose results are quoted. The reviewer recognizes that even in a number of the original publications such references are also lacking.

The monograph concludes with a splendid bibliography, alphabetically arranged according to authors. This bibliography could be more readily used had the references been included at the end of the various chapters.

This volume fills a long-felt need in our American chemical literature, and will be indispensable to all investigators desiring authoritative information on the chemistry of wheat flour. The author's suggestion as to the need for a monograph devoted to the biochemistry of baking is most timely. Such a publication would furnish a most excellent supplement to the present volume.

F. C. Blanck

GOVERNMENT PUBLICATIONS

Notice—*Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the bureau or department from which they originate.*

Bureau of Foreign and Domestic Commerce

Plans for the Production of Synthetic Methanol in France. *Special Circular* 113, Chemical Division. 3 pp. Issued July 25, 1925.

Possibilities for Para Rubber Production in the Philippine Islands. C. F. Vance, A. H. Muzzall, J. P. Bushnell, and Mark Baldwin. *Trade Promotion Series* 17. 101 pp. Paper, 20 cents.

The French Fertilizer Trade during 1924. *Special Circular* 108, Chemical Division. 3 pp. Issued July 20, 1925.

The Market for Fertilizers in Salvador. *Special Circular* 115, Chemical Division. 4 pp. Issued July 27, 1925.

World Trade Notes on Coal-Tar Products. *Circular* 68-B, Chemical Division. 2 pp. Issued August 29, 1925.

World Trade Notes on Fertilizers. *Circular* 68-E, Chemical Division. 2 pp. Issued August 29, 1925.

World Trade Notes on Industrial Chemicals. *Circular* 68-A, Chemical Division. 3 pp. Issued August 29, 1925.

World Trade Notes on Paints and Naval Stores. *Circular* 68-D, Chemical Division. 1 p. Issued August 29, 1925.

Bureau of Mines

Cleaning Tests of Central Illinois Coal. Thomas Fraser and H. F. Yancey. *Technical Paper* 361. 23 pp. Paper, 5 cents.

Mine Timber: Its Selection, Storage, Treatment, and Use. R. R. Hornor and H. E. Tufft. **With a Chapter on Methods of Prolonging Life of Mine Timber.** G. M. Hunt. *Bulletin* 235. 118 pp. Paper, 30 cents.

Permissible Explosives, Mining Equipment, and Rescue Apparatus Approved Prior to January 1, 1925. J. E. Crawshaw, L. C. Ilsley, D. J. Parker, and A. C. Fieldner. *Technical Paper* 376. 35 pp. Paper, 5 cents.

Production of Explosives in the United States during the Calendar Year 1924 with Notes on Mine Accidents Due to Explosives. W. W. Adams. *Technical Paper* 380. 35 pp. Paper, 5 cents.

Screen Sizing of Coal, Ores, and Other Minerals. E. A. Holbrook and Thomas Fraser. *Bulletin* 234. 140 pp. Paper, 40 cents.

Small Hose Streams for Fighting Mine Fires. L. D. Tracy and R. W. Hendricks. *Technical Paper* 330. 23 pp. Paper, 10 cents.

Bureau of Standards

A Method of Determining the Dew Points of Fuel-Air Mixtures. R. J. Kennedy. *Scientific Paper* 500. Paper, 10 cents.

A Method of Studying Electrode Potentials and Polarization. H. D. Holler. *Scientific Paper* 504. Paper, 15 cents.

Comparative Durability of Chrome and Vegetable Tanned Sole Leathers. R. C. Bowker and M. N. V. Geib. *Technologic Paper* 286. 20 pp. Paper, 10 cents.

Comparative Slow Bend and Impact Notched Bar Tests on Some Metals. S. N. Petrenko. *Technologic Paper* 289. 32 pp. Paper, 20 cents.

Comparative Wearing Qualities of Pima and Ordinary Cotton Used in Mail Bags. F. R. McGowan, C. W. Schoffstall, and A. A. Mercier. *Technologic Paper* 277. Paper, 10 cents.

Malleability and Metallography of Nickel. P. D. Merica and R. G. Waltenberg. *Technologic Paper* 281. Paper, 10 cents.

Reclamation of Gasoline Used in Dry-Cleaning. C. C. Hubbard. *Technologic Paper* 280. Paper, 5 cents.

Tables and Graphs for Facilitating the Computation of Spectral Energy Distribution by Planck's Formula. *Miscellaneous Publication* 56. Paper, 35 cents.

United States Government Master Specification for Asbestos Metallic Cloth Sheet Packing. *Circular* 243. 3 pp. Paper, 5 cents.

Same. Cotton Waste, Colored. *Circular* 263. 3 pp. Paper, 5 cents.

Same. Cotton Waste, White. *Circular* 262. 3 pp. Paper, 5 cents.

Same. Rubber Goods (Methods of Physical Tests and Chemical Analyses). *Circular* 232. 42 pp. Paper, 10 cents

Same. Rubber Valves. *Circular* 244. 3 pp. Paper, 5 cents.

Same. Wool Waste, Colored. *Circular* 260. 3 pp. Paper, 5 cents.

Department of Agriculture

A Study of Essential Plant Foods Recoverable from the Manure of Dairy Cows. C. F. Wells and B. A. Dunbar. *Journal of Agricultural Research*, 30 (May 15, 1925), 985–8.

Effect of Seeds upon Hydrogen-Ion Concentration Equilibrium in Solution. Willem Rudolfs. *Journal of Agricultural Research*, 30 (June 1, 1925), 1021–6.

Extension Work in Foods and Nutrition, 1923. Miriam Birdseye. *Department Circular* 349. 31 pp. Paper, 5 cents.

Feeding Chlorinated Milk to the Albino Rat. J. W. Read and Harrison Hale. *Journal of Agricultural Research*, 30 (May 1, 1925), 889–92.

Microörganisms in Decomposing Oysters. A. C. Hunter and V. A. Linden. *Journal of Agricultural Research*, 30 (May 15, 1925), 987–93.

Physiological and Biochemical Studies on Cereals. IV—On the Presence of Amino Acids and Polypeptides in the Ungerminated Rye Kernel. S. L. Jodidi and J. G. Wangler. *Journal of Agricultural Research*, 30 (May 15, 1925), 987–94.

Geological Survey

Bauxite and Aluminium in 1924. J. M. Hill. *Mineral Resources of the United States, 1924.* Part I, pp. 21–9. Published August 4, 1925.

Cadmium in 1923–1924. C. E. Siebenthal and A. Stoll. *Mineral Resources of the United States, 1924.* Part I, pp. 7–11.

Gold, Silver, Copper, Lead, and Zinc in New Mexico and Texas in 1923. Mine Report. C. W. Henderson. *Mineral Resources of the United States, 1923.* Part I, pp. 593–609. Published July 30, 1925.

Mineral Resources of the United States in 1924. (Summary Report.) Introduction by F. J. Katz. Statistics assembled by M. B. Clark. 108 pp. Published August 10, 1925.

Mineral Resources of the United States, 1922. Part I—Metals. G. F. Loughlin. 648 pp. Cloth, $1.00.

Peat in 1924. K. W. Cottrell. *Mineral Resources of the United States, 1924.* Part II, pp. 11–2. Published July, 1925.

Petroleum in 1923. G. B. Richardson. *Mineral Resources of the United States, 1923.* Part II, pp. 365–420. Published August 27, 1925.

Petroleum on Alaska Peninsula. Papers by K. F. Mather, W. R. Smith, and G. C. Martin. *Bulletin* 773-D. 55 pp.

Quicksilver in 1924. C. P. Ross. *Mineral Resources of the United States, 1924.* Part I, pp. 13–9. Published July 30, 1925.

Surface Water Supply of the United States, 1921. Part IX—Colorado River Basin. N. C. Grover, Robert Follansbee, A. B. Purton, and R. C. Rice. *Water-Supply Paper* 529. 181 pp. Paper, 25 cents.

Surface Water Supply of the United States, 1921. Part XII—North Pacific Slope Drainage Basins. C. Lower Columbia River Basin and Pacific Slope Drainage Basins in Oregon. N. C. Grover, F. F. Henshaw, and G. L. Parker. *Water-Supply Paper* 534. 171 pp. Paper, 20 cents.

Surface Water Supply of the United States, 1921. Part II—South Atlantic Slope and Eastern Gulf of Mexico Basins. N. C. Grover, A. H. Horton, G. C. Stevens, and W. E. Hall. *Water-Supply Paper* 522. 72 pp. Paper, 10 cents.

Surface Water Supply of the United States, 1922. Part IV—St. Lawrence River Basin. N. C. Grover, S. B. Soule, A. H. Horton, Lasley Lee, C. C. Covert, A. W. Harrington, and C. H. Pierce. *Water-Supply Paper* 544. 140 pp.

Tin in 1924. B. L. Johnson. *Mineral Resources of the United States, 1924.* Part I, pp. 31–3. Published August 7, 1925.

Public Health Service

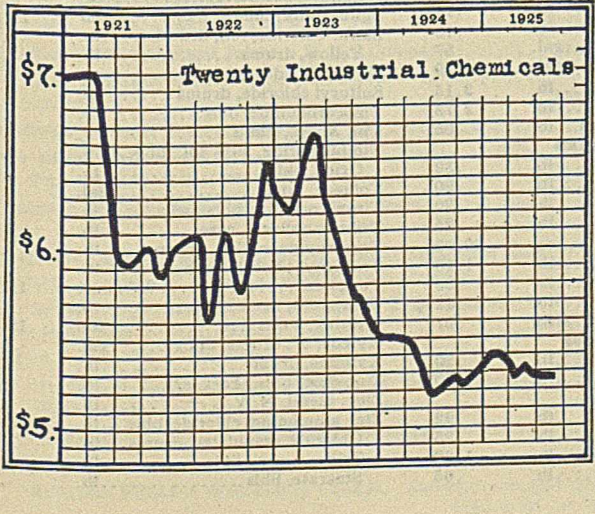
Some Specific Factors Responsible for Pollution or Affecting Analyses of Water Supplies. Reprint 972 from *Public Health Reports.* 4 pp. Paper, 5 cents.

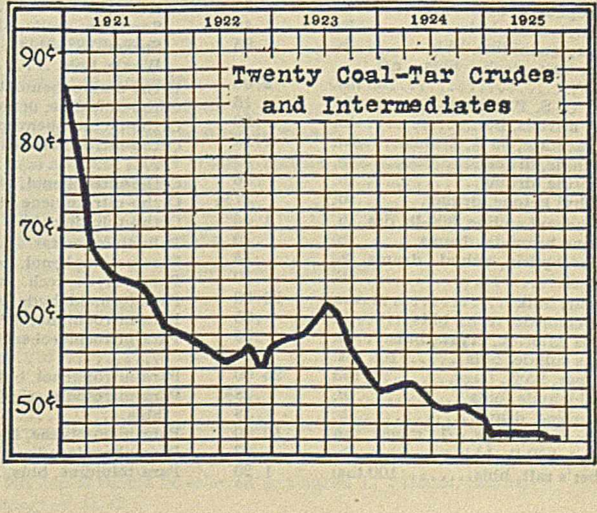
Studies on the Industrial Dust Problem. III—Comparative Field Studies of the Palmer Apparatus, the Konimeter, and the Impinger Methods for Sampling Aerial Dust. Leonard Greenburg. *Public Health Reports*, 40 (July 31, 1925), 1591–1603.

MARKET REPORT—SEPTEMBER, 1925

FIRST-HAND PRICES FOR CHEMICALS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET ON SEPTEMBER 15

Acetanilide, tech., bbls	lb.	.27
U. S. P., bbls	lb.	.35
Acetic anhydride, 92–95%, cbys.	lb.	.37
Acetone, C. P., drums, wks.	lb.	.13
Acetophenetidine, bbls	lb.	1.85
Acid, Acetic, 28%, c/l. bbls.	100 lbs.	3.00
56%, c/l. bbls	100 lbs.	5.60
Glacial, c/l. bbls	100 lbs.	10.57
Acetylsalicylic, bbls	lb.	.72½
Anthranilic, 99–100%, drums	lb.	.98
Benzoic, tech., bbls	lb.	.57
Boric, bbls	lb.	.09½
Butyric, 60%, pure, 5-lb. bot.	lb.	.55
Chloroacetic, mono-, bbls., wks.	lb.	.25
Di-, cbys	lb.	1.00
Tri-, bbls	lb.	2.50
Chlorosulfonic, drums, wks.	lb.	.15
Chromic, pure, 85%, drums	lb.	.35
Chromotropic, bbls	lb.	1.35
Cinnamic, 5-lb. cans	lb.	3.25
Citric, U. S. P., kegs, bbls	lb.	.46
Cresylic, pale, drums	lb.	.54
Formic, 85%, cbys., N. Y.	lb.	.10
Gallic, U. S. P., bbls	lb.	.65
Glycerophosphoric, 25%, 1-lb. bot	lb.	1.85
H, bbls., wks	lb.	.68
Hydriodic, 10%, U. S. P., 5-lb. bot	lb.	.65
Hydrobromic, 48%, cbys., wks.	lb.	.45
Hydrochloric, 20°, tanks, wks	100 lbs.	1.00
Hydrofluoric, 30%, bbls., wks.	lb.	.06
60%, bbls., wks	lb.	.13
Hydrofluosilicic, 35%, bbls., wks	lb.	.10
Hypophosphorous, 30%, U. S. P., 5-gal. demis	lb.	.36
Lactic, 22%, dark, bbls	lb.	.05½
Lactic, 66%, light, bbls., wks	lb.	.26
Metanilic, bbls	lb.	.60
Mixed, tanks, wks	N unit	.06
	S unit	.01
Molybdic, 85%, kegs	lb.	1.25
Naphthionic, tech., bbls	lb.	.55
Neville & Winther's, bbls	lb.	.95
Nitric, C. P., cbys	lb.	.12
Nitric, 38°, c/l. cbys., wks.	100 lbs.	5.00
Oxalic, bbls., wks	lb.	.11
Phosphate, bulk	ton	9.50
Phosphoric, 50%, cbys	lb.	.07
Picramic, bbls	lb.	.50
Picric, bbls	lb.	.26
Pyrogallic, tech., bbls	lb.	.85
Salicylic, tech., bbls	lb.	.33
Stearic, d. p., bbls	lb.	.14¾
Sulfanilic, 250-lb. bbls	lb.	.15
Sulfuric, 66°, c/l. cbys., wks.	100 lbs.	1.25
66°, tanks, wks	ton	14.00
60°, tanks, wks	ton	9.50
Oleum, 20%, tanks, wks	ton	17.00
40%, tanks, wks	ton	40.00
Sulfurous, U. S. P., 6%, cbys	lb.	.05
Tannic, tech., bbls	lb.	.30
Tartaric, U. S. P., cryst., bbls	lb.	.29
Tobias, bbls	lb.	.85
Tungstic, kegs	lb.	1.00
Valeric, C. P., 10-lb. bot	lb.	2.50
Alcohol, U. S. P., 190 proof, bbls	gal.	4.94
Cologne Spirit, bbls	gal.	5.04
Amyl, 10%, Imp. drums	gal.	2.20
Butyl, drums, wks	lb.	.24½
Denatured, No. 5, Comp. denat., drs	gal.	.53½
No. 6, Comp. denat., drs	gal.	.52½
No. 1, Spec. denat., drs	gal.	.53½
Isobutyl, ref., drums	lb.	1.10
Isopropyl, ref., drums	gal.	1.00
Propyl, ref., drums	lb.	.75
Wood, *see* Methanol		
Alpha-naphthol, bbls	lb.	.65
Alpha-naphthylamine, bbls	lb.	.35
Alum, ammonia, lump, bbls., wks	100 lbs.	3.15
Chrome, casks, wks	100 lbs.	5.25
Potash, lump, bbls., wks.	100 lbs.	3.50
Soda, bbls., wks	100 lbs.	3.50
Aluminium, metal, N. Y.	lb.	.27
Aluminium chloride, anhyd., drums	lb.	.20
Aluminium stearate, 100-lb. bbl.	lb.	.22
Aluminium sulfate, comm'l, bags, wks	100 lbs.	1.40
Iron-free, bags, wks	100 lbs.	2.00
Amidopyrine, boxes	lb.	4.60
Aminoazobenzene, 110-lb. kgs	lb.	1.15
Ammonia, anhydrous, cyl., wks.	lb.	.30
Ammonia water, 26°, drums, wks	lb.	.06½
Ammonium acetate, kegs	lb.	.43
Bifluoride, bbls	lb.	.21
Bromide, 50-lb. boxes	lb.	.53
Carbonate, tech., casks	lb.	.08¾
Chloride, gray, bbls	lb.	.07¾
Lump, casks	lb.	.10½
White, bbls	lb.	.07
Iodide, 25-lb. jars	lb.	5.20
Lactate, bbls	lb.	.15
Nitrate, tech., cryst., bbls	lb.	.21
Oxalate, kegs	lb.	.35
Persulfate, cases	lb.	.28
Phosphate, dibasic, tech., bbls	lb.	.18
Tribasic, bbls	lb.	.04
Sulfate, bulk, wks	100 lbs.	2.85
Thiocyanate, tech., kegs	lb.	.40
Amyl acetate, tech., drums	lb.	2.65
Aniline oil, drums	lb.	.16
Anthracene, 80–85%, casks, wks.	lb.	.60
Anthraquinone, subl., bbls	lb.	.95
Antimony, metal	lb.	.16¾
Antimony chloride, anhyd., drums	lb.	.35
Oxide, bbls	lb.	.17½
Salt, Dom., bbls	lb.	.26
Sulfide, crimson, bbls	lb.	.26
Golden, bbls	lb.	.16
Vermilion, bbls	lb.	.48
Tartrolactate, bbls	lb.	.45
Argols, red powder, bbls	lb.	.06½
Arsenic, metal, kegs	lb.	.45
Red, kegs, cases	lb.	.13
White, cases, bbls	lb.	.03½
Asbestine, bulk, c/l	ton	16.00
Barium carbonate, bbls., bags, wks	ton	50.00
Chloride, bbls., bags, wks	ton	60.00
Dioxide, bbls., wks	lb.	.13
Hydroxide, bbls	lb.	.04½
Nitrate, casks	lb.	.07½
Barium sulfocyanide, 400-lb. bbls	lb.	.30
Barytes, floated, 350-lb. bbls., wks	ton	26.00
Benzaldehyde, tech., drums	lb.	.70
F. F. C., cbys	lb.	1.40
U. S. P., cbys	lb.	1.15
Benzene, pure, tanks, mills	gal.	.25
Benzidine base, bbls	lb.	.75
Benzoyl chloride, carboys	lb.	1.00
Benzyl acetate, cbys	lb.	1.55
Alcohol, 5-liter bot.	lb.	1.45
Chloride, tech., drums	lb.	.25
Beta-naphthol, bbls	lb.	.24
Beta-naphthylamine, bbls	lb.	.63
Bismuth, metal, cases	lb.	2.95
Bismuth nitrate, 25-lb. jars	lb.	2.00
Oxychloride, boxes	lb.	3.50
Subnitrate, U. S. P., 25-lb. jars	lb.	2.75
Blanc fixe, dry, bbls	ton	75.00
Bleaching powder, drums, wks.	100 lbs.	1.90
Bone ash, kegs	lb.	.06
Bone black, bbls	lb.	.08¼
Borax, powd., bbls	lb.	.05





Bordeaux mixture, bbls.........lb.	.11¾
British gum, com., c/l......100 lb.	4.72
Bromine, bot...................lb.	.47
Bromobenzene, drums..........lb.	.50
Bromoform, 5-lb. bot..........lb.	1.65
Butyl acetate, 100-gal. drums..gal.	2.04
Cadmium bromide, 50-lb. jars...lb.	1.20
Cadmium, metal, boxes.........lb.	.70
Cadmium sulfide, cs............lb.	1.20
Caffeine, U. S. P., 5-lb. cans....lb.	3.75
Calcium acetate, bags......100 lbs.	2.75
Arsenate, bbls................lb.	.06½
Carbide, drums...............lb.	.04¼
Chloride, drums, wks.... 100 lbs.	21.00
Lactate, tech., bbls...........lb.	.35
Nitrate, bbls..................ton	50.00
Phosphate, monobas., bbls....lb.	.07
Tribas., bbls................lb.	.11
Calcium carbonate, tech., bgs. 100 lb.	1.10
U. S. P., precip., 175-lb. bbl...lb.	.06½
Camphor, Amer., bbls..........lb.	.84
Jap., cases...................lb.	.75
Crude, cases ....lb.	.54
Camphor, monobrom, cs........lb.	1.85
Caramel, bbls..................gal.	.85
Carbazole, bbls.................lb.	.50
Carbon bisulfide, drums........lb.	.06
Carbon black, cases............lb.	.12
Carbon dioxide, liq., cyl........lb.	.06
Carbon tetrachloride, drums.....lb.	.07
Casein, tech., bbls.............lb.	.13
Cellulose acetate, cs............lb.	2.00
Cerium oxalate, kegs...........lb.	.35
Chalk, pptd., casks.............lb.	.04¼
Charcoal, willow, powd., bbls...lb.	.06
China clay, imp., bgs......100 lbs.	15.00
Chloral hydrate, drums.........lb.	.60
Chloramine T., 5-lb. bot........lb.	1.35
Chlorcosane, 5-lb. bot..........lb.	.55
Chlorohydrin, anhyd., drums....lb.	.75
Chlorine, liq., c/l, cyl...........lb.	.05½
Chlorobenzene, mono-, drums...lb.	.08
Chloroform, tech., drums ....lb.	.28
Chromium acetate, 20° sol., bbls..lb.	.05½
Sulfate, bbls..................lb.	.07
Cinchonidine sulfate, 100 oz.....oz.	.35
Coal tar, tanks, bbls., wks.....gal.	.07
Cobalt, metal, kegs.............lb.	2.50
Cobalt oxide, bbls..............lb.	2.10
Cod-liver oil, bbls.............bbl.	43.00
Collodion, drums...............lb.	.23
Copperas, c/l., bulk ....ton	13.00
Copper, metal, elec.............lb.	.14¾
Copper carbonate, bbls.........lb.	.16¾
Chloride, bbls.................lb.	.28
Cyanide, drums...............lb.	.48
Oxide, red, bbls...............lb.	.16½
Sulfate, bbls..................lb.	.04½
Cotton, soluble, bbls...........lb.	.40
Cream tartar, bbls..............lb.	.22
Cyanamide, bulk, N. Y. ....Ammon. unit	1.90
Diaminophenol, kegs...........lb.	3.80
Dianisidine, kegs...............lb.	3.50
Dichlorobenzene, drums........lb.	.06
Diethylaniline, drums...........lb.	.55
Diethyl phthalate, drums.......lb.	.35
Diethyl sulfate, tech., drums....lb.	.20
Dimethylaniline, drums.........lb.	.32
Dimethylsulfate, drums.........lb.	.50
Dinitrobenzene, drums..........lb.	.14½
Dinitrochlorobenzene, bbls......lb.	.15
Dinitronaphthalene, bbls........lb.	.32
Dinitrophenol, bbls.............lb.	.32
Diphenylamine, bbls............lb.	.48
Diphenylguanidine, bbls........lb.	.95
Epsom salt, tech., bbls., c/l, N. Y...................100 lbs.	2.00
Ether, U. S. P., drums..........lb.	.16
Ether, nitrous, bot..............lb.	.90
Ethyl acetate, 99%, drums.....gal.	1.15
Bromide, drums...............lb.	.50
Chloride, drums...............lb.	.26
Methyl ketone, drums........lb.	.27½
Ethyl benzyl aniline, 300-lb. drs..lb.	1.05
Ethylene bromide, drums ....lb.	.70
Chlorohydrin, anhyd., drums..lb.	.75
Glycol.......................lb.	.30
Feldspar, bulk..................ton	20.00
Ferric chloride, tech., bbls......lb.	.05
Ferrous chloride, cryst., bbls....lb.	.05
Ferrous sulfide, bbls.......100 lbs.	2.50
Fluorspar, 95%, bags..........ton	25.00
Formaldehyde, bbls.............lb.	.08¾
Formaniline, drums.............lb.	.38
Fuller's earth, bags, c/l., mines . ton	15.00
Furfural, 300-lb. bbls...........lb.	.23
Glauber's salt, bbls........100 lbs.	1.20
Glucose, 70°, bags, dry.....100 lbs.	3.69
Glycerol, C. P., drums..........lb.	.19
G salt, bbls.....................lb.	.50
Hexamethylenetetramine, drums.lb.	.60
Hydrogen peroxide, 25 vol., bbls.........................lb.	.07
Hydroquinone, kegs............lb.	1.40
Indigo, 20% paste, bbls.........lb	.14
Iodine, crude, 200-lb. kgs....... lb.	4.20
Iodine, resubl., jars.............lb.	4.65
Iodoform, bot...................lb.	6.00
Iridium, metal..................oz.	260.00
Kieselguhr, bags...............ton	60.00
Lead, metal.....................lb.	.09½
Lead acetate, bbls. white.......lb.	.15½
Arsenate, bbls...............lb.	.13
Oxide, litharge, bbls..........lb.	.11½
Red, bbls..................lb.	.12
Peroxide, drums..............lb.	.25
White, basic carb., bbls.......lb.	.10¾
Sulfate, bbls...............lb.	.10
Lime, live, chemical, bbls., wks. ....100 lbs.	1.05
Lime, hydrated, bbls...... 100 lbs.	.85
Limestone, ground, bags, wks...ton	4.50
Lithium carbonate, 100-lb. kgs...lb.	1.45
Lithopone, bbls..................lb.	.06⅛
Magnesite, crude...............ton	15.00
Calcined, 500-lb. bbls., wks..ton	48.00
Magnesium, metal sticks, wks...lb.	.85
Magnesium carbonate, bags.....lb.	.06¾
Chloride, drums..............ton	34.00
Fluosilicate, cryst., bbls.......lb.	.12
Oxide, U. S. P., light, bbls....lb.	.42
Manganese chloride, casks......lb.	.06
Dioxide, 80%, bbls..........ton	80.00
Sulfate, casks................lb.	.07
Mercury bichloride, cryst., 25 lbs.lb.	1.20
Mercury, flasks, 75 lb.........flask	81.00
Meta-nitroaniline, bbls..........lb.	.73
Meta-phenylenediamine, bbls....lb.	.85
Meta-toluylenediamine, bbls....lb.	.73
Methanol, 97%, tanks.........gal.	.57
Methyl acetone, drums.........gal.	.83
Salicylate, cases.............lb.	.43
Methyl chloride, cylinders......lb.	.50
Michler's ketone, bbls...........lb.	3.00
Monoethylaniline, drums.......lb.	1.05
Naphtha, solvent, tanks.......gal.	.26
Naphthalene, flake, bbls........lb.	.04½
Nickel, metal....................lb.	.34
Nickel salt, single, bbls.........lb.	.08
Double, bbls..................lb.	.08½
Niter cake, bulk...............ton	4.50
Nitrobenzene, drums............lb.	.09½
Oil, castor, No. 1...............lb.	.16
China wood, bbls............lb.	.13½
Coconut, Ceylon, tanks.......lb.	.11
Cod, N. F., tanks...........gal.	.55
Corn, crude, tanks...........lb.	.10
Cottonseed, crude, tanks......lb.	.09⅜
Lard, edible, bbls............lb.	.20
Linseed, bbls................gal.	1.03
Menhaden, crude, tanks.....gal.	.52
Neat's-foot, pure, bbls........lb.	.14¾
Oleo, No. 1, bbls.............lb.	.17
Olive oil, denat., bbls........gal.	1.20
Foots, bbls.................lb.	.08⅞
Palm, Lagos, bbls............lb.	.09
Peanut, crude, tanks.........lb.	.10½
Perilla, bbls..................lb.	.15¼
Rapeseed, bbls..............gal.	1.02
Red, bbls....................lb.	.11¾
Soy bean, crude, bbls.........lb.	.13
Sperm, 38°, bbls............gal.	.87
Whale, bbls.................gal.	.79
Ortho-aminophenol, kegs........lb.	2.15
Ortho-anisidine, drums.........lb.	2.75
Ortho-dichlorobenzene, drums...lb.	.06
Ortho-nitrochlorobenzene, drums ....lb.	.32
Ortho-nitrophenol, bbls.........lb.	.90
Ortho-nitrotoluene, drums......lb.	.20
Ortho-toluidine, bbls............lb.	.25
Palladium, metal...............oz.	80.00
Para-aminophenol, kegs.........lb.	1.10
Paraldehyde, tech., drums......lb.	.30
Para-formaldehyde, cases.......lb.	.42½
Para-nitroaniline, bbls..........lb.	.57
Para-nitrochlorobenzene, drums ....lb.	.20
Para-nitrophenol, bbls..........lb.	.50
Para-nitrosodimethylaniline, bbls.........................lb.	.92
Para-nitrotoluene, bbls.........lb.	.35
Para-phenylenediamine, bbls....lb.	1.20
Para-toluidine, bbls............lb.	.65
Paris Green, 500-lb. kgs.........lb.	.19
Phenol, drums..................lb.	.21
Phenolphthalein, drums.........lb.	1.30
Phenylethyl alcohol, 1-lb. bot....lb.	7.00
Phosphorus, red, cases..........lb.	.70
Phosphorus trichloride, cyl......lb.	.45
Phthalic anhydride, bbls........lb.	.18
Platinum, metal.................oz.	80.00
Potash, caustic, drums..........lb.	.07⅛
Potassium acetate, kegs.........lb.	.29
Bicarbonate, casks...........lb.	.09
Bichromate, casks............lb.	.08½
Binoxalate, bbls..............lb.	.16
Bromate, cs..................lb.	.85
Carbonate, 80–85%, calc., casks.....................lb.	.05¾
Chlorate, kegs...............lb.	.08½
Chloride....................ton	34.55
Cyanide, cases ....lb.	.55
Meta-bisulfite, bbls..........lb.	.10
Permanganate, drums........lb.	.14½
Prussiate, red, casks.........lb.	.37½
Yellow, casks.............lb.	.18½
Titanium oxalate, bbls.......lb.	.21
Pyridine, drums...............gal.	4.50
Quinine bisulfate, 100 oz.......oz.	.45
Sulfate, 100-oz. cans.........oz.	.50
Resorcinol, tech., kegs..........lb.	1.35
Rochelle salt, bbls., U. S. P......lb.	.19
R salt, bbls.....................lb.	.45
Saccharin, cans.................lb.	1.75
Salt cake, bulk.................ton	19.00
Saltpeter, gran., bbls...........lb.	.06¼
Silica, ref., bags................ton	18.00
Silver nitrate, 16-oz. bot.........oz.	.48½
Soda ash, 58%, light, bags, contract, wks..............100 lbs.	1.38
Soda, caustic, 76%, solid, drums, contract, wks.....100 lbs.	3.10
Sodium acetate, bbls............lb.	.04½
Benzoate, bbls...............lb.	.50
Bicarbonate, bbls........100 lbs.	2.00
Bichromate, casks............lb.	.06⅝
Bisulfite, bbls................lb.	.04
Bromide, bbls................lb.	.48
Carbonate, sal soda, bbls., 100 lbs.	1.30
Chlorate, kegs................lb.	.06½
Chloride, bags...............ton	12.00
Cyanide, cases...............lb.	.20
Fluoride, bbls................lb.	.08¾
Hyposulfite, reg., crys., bbls..lb.	.02½
Metallic, drums, 12¼-lb. bricks lb.	.27
Naphthionate, bbls...........lb.	.55
Nitrate, crude, bags, N. Y. ....100 lbs.	2.50
Nitrite, bbls..................lb.	.09
Perborate, bbls...............lb.	.21
Peroxide, cases..............lb.	.27
Phosphate, trisod............lb.	.03¾
Picramate, kegs..............lb.	.60
Prussiate, bbls...............lb.	.10½
Silicate, drums, tanks, 40°, 100 lbs.	.75
Silicofluoride, bbls...........lb.	.04¼
Stannate, drums ....lb.	.40
Sulfate, anhyd., bbls.........lb.	.02½
Sulfide, cryst., bbls..........lb.	.02½
Solid, 60%................lb.	.04
Sulfocyanide, bbls............lb.	.30
Tungstate, kegs..............lb.	.70
Strontium carbonate, bbls.......lb.	.07
Nitrate, bbls.................lb.	.07½
Strychnine alkaloid, 100 oz., powd. oz.	.71
Sulfate, powder..............oz.	.50
Sulfur, bulk, mines, wks.......ton	14.00
Sulfur chloride, red, drums......lb.	.05½
Yellow, drums...............lb.	.04½
Sulfur dioxide, cyl..............lb.	.08
Sulfuryl chloride, drums........lb.	.65
Thiocarbanilide, bbls...........lb.	.24
Tin, Amer., stand..............lb.	.58¼
Tin bichloride, 50% sol., bbls....lb.	.16
Oxide, bbls..................lb.	.61
Toluene, tanks.................gal.	.26
Titanium oxide, bbls., wks.......lb.	.13
Tribromophenol, cases..........lb.	1.10
Triphenylguanidine, drums......lb.	.69
Triphenyl phosphate, bbls.......lb.	.75
Tungsten................WO_3 unit	11.50
Urea, pure, cases...............lb.	.18
Whiting, bags..................ton	18.00
Xylene, 5°, drums, mills.......gal.	.40
Xylidine, drums................lb.	.37
Zinc dust, bbls., kegs, c/l.......lb.	.09
Zinc, metal, N. Y...............lb.	.07½
Zinc ammonium chloride, bbls....lb.	.06¼
Chloride, granulated, drums...lb.	.07
Oxide, Amer., bbls............lb.	.07⅜
Stearate, bbls................lb.	.21