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The First Generation

With the present year the first generation of the twentieth century will have passed into history, and it has therefore seemed to us worth while to offer the results of a little stock-taking in this issue of Industrial and Engineering Chemistry. This we have endeavored to do through a group of special articles in which will be found discussed the best practice now prevailing in the design and construction of certain chemical equipment. The story is by no means complete, and in subsequent issues we plan to present additional discussions along the same line. Here and there will be found reference to difficulties still to be overcome by the equipment manufacturer to meet the specifications of the chemical and allied industries. Also trends are indicated which may suggest to those in research and development work fruitful lines for their investigation.

It is rather fascinating to think over and note what has been accomplished in chemistry and the chemical industry since so recent a date as 1900. Commercial achievements based upon research conducted within that time comprise a list startling in its magnitude and significance, and encouraging as indicating how the possibilities unfold as our stock of truth accumulates. The influence upon our habits of thinking is undisputed and the next generation will see many things accomplished which even the present has hesitated to undertake, deterred by the apparent impossibility of success.

Responsibility for Hazards

The effort to have the duty on sodium chlorate removed on the ground that it is useful and effective in destroying harmful weeds on the farms has brought to our attention a situation which borders on the appalling, when one considers the hazards involved in the use of this material and the responsibility of those who have urged it upon men not technically trained. It is not surprising that tariff revision for agricultural benefit should be made the occasion to seek the removal of duty on this material, but it seems to us that these are unrelated matters. Sodium chlorate, among other materials for weed eradication, has been used with considerable success on railroad rights of way, but here methods of applying the material can be standardized and carried out under the supervision of those who know the hazards with which they are dealing and can take suitable precautions. But think of the potential menace to life and property when an open keg or drum of chlorate is stored in the old barn, where it may readily come in contact with organic dusts. Think of the hazards that remain after its use, even though the exceptional farmer may have taken the trouble to read the warning label on the container.

There is no difficulty in storing sodium chlorate safely under standardized conditions, and warehouses have no trouble about insurance, for they know what precautions should be taken. But it seems to us that all of this changes when the package is opened on the farm.

We are informed that many thousands of dollars of damage have already resulted from the use of this chemical in the fields. In one instance, a few days after the application of sodium chlorate a man was walking through the area that had been sprayed. The sun was hot, the plot was dry, and suddenly the man found himself on a bed of fire. Luckily he lost no more than the cuffs of his trousers. The same day the vehicle that had been used to carry the solution and spraying equipment was being driven along a road. The men on the wagon were startled to find the rear end on fire, probably caused by the intense heat of the sun or the jar and friction on the wagon boards where the sodium chlorate had dried in the wood. There have been other cases where the chemical dried on the clothing of those applying it and later burst into flame, causing serious burns. Buildings have been destroyed by fire apparently resulting where the solution dried or where dusts accumulated with the chlorate.

Sodium chlorate, may we reiterate, packed according to standard practice in metal containers, is safe as long as it remains in those containers, and of itself is not dangerous, inflammable, or explosive. It acquires these undesirable characteristics so far as the farm is concerned when mixed with organic or other combustible matter, and every precaution has to be taken, therefore, to prevent such admixture.

In view of these well-known facts, it seems to us exceedingly strange that some agronomists, county agents, and experiment station men should have shared in the responsibility of advocating the use of so hazardous a material in the hands of inexperienced operators. Labels may give legal protection, but there is an abundance of proof that "caution," "warning," "poison," and other sorts of labels are seldom carefully read, and sometimes the truth of their statements is not appreciated. Methanol affords another example.

An incidental objection to sodium chlorate on the farm arises from the probable decomposition of that salt into its equivalent of harmful sodium chloride. A quantity of chlorate sufficient to kill prevailing weeds thus would ruin some soils in the dry farming region. This menace is, of course, insignificant as compared with the more serious one—danger to both life and property in the storage of chlorate in open containers, where dust and other combustible matter may easily come in contact with it.

By all means let us do our utmost to overcome weeds. We can begin with clean seeds and an educational campaign to convince the farmer how much he loses if weeds are allowed to flourish. But let us not destroy the farm and burn down its buildings, thereby emulating those who would burn down the house to destroy the rats. Our friends who are advising agricultural folk can always without great difficulty obtain the advice and coöperation of their colleagues in chemistry. Such contacts will greatly further the desirable application of chemistry to farm work and eliminate unnecessary hazards.

Uncle John's Sermon

IN THE impressive series of monographs sponsored by the AMERICAN CHEMICAL SOCIETY, the fiftieth of which is now being announced, one would not expect to find a sermon to chemists. But our Treasurer, John E. Teeple, in his discussion of the industrial development of Searles Lake brines, fortunately includes a number of interesting things, among which we find a sermon for the younger men.

The text has been found in some of the special features of the difficult problem presented in the utilization of Searles Lake. Even those who are not particularly interested in the separation of so complex a mixture of salts as this dry pocket presents would do well to read that part of the monograph which gives the history of the development and the difficulties overcome.

Doctor Teeple clearly sets out his basis for distinguishing between the chemist, the chemical engineer, the physical chemist, and the physicist, classifying them according to "the amount of material they need to have in hand in order to be at their very best level of thought." He says the chemist does best when working in grams, the chemical engineer demands tons, the physical chemist "is one who works best and thinks best with molecules rather than grams or tons, probably not to exceed ten or a dozen molecules at one time, and the modern physicist is at his very best inside the spacious confines of a single atom."

Now for the sermon, penned out of Doctor Teeple's extensive and varied experience:

> My lecture to young men who are about to assume a position giving them some authority over other technical men runs about as follows:
>
> (1) Don't strut; the fact that you now have a certain title or position is extremely unimportant to everyone but yourself. It doesn't prove anything. Maybe in selecting you some one made a mistake which will be rectified later. The essential thing is, what can you do, what can you contribute, how much better are you than a vacancy in the office? Crazy Ludwig was king of Bavaria, and Caligula's horse was consul of Rome. These were important events to Ludwig and maybe to the horse, but they can hardly be counted as factors in successful progress.
>
> (2) Never hesitate to make a decision. Never pass it up to your superiors unless it involves factors quite outside your province and beyond your control which might adversely affect other departments. Likewise insist on your subordinates making their own decisions whenever humanly possible. It may make you feel tremendously important to hold conferences and issue edicts, but it isn't good for the men, nor in the long run is it good for the business. Help them whenever you can, advise with them on matters where your judgment or experience may be better than theirs, see that they have the vision of what you are aiming at, but be very chary about issuing orders, and never place responsibility on a man without at the same time giving him adequate authority. Have a genuine respect for other men who are really doing anything, whether your subordinates, associates or superiors. Every one of them is probably a better and abler man than you are in some particular kind of work. See to it that there is some work that you do better than any of them in order to maintain their respect, too. The man who has not a real appreciation for the work of other men should be allowed to depart from an organization quietly and quickly.
>
> (3) Don't overwork the push button, and don't be a fusser. When men are on the carpet in your office they are not doing the work for which they are paid, and weeks afterwards they may be resenting unfair things you said, instead of doing constructive work.
>
> (4) Play fair; no alibis. If something goes wrong don't hesitate to take the blame. We can forgive honest mistakes when a man tries to do something. What we can't forgive is the mistake of the man who is afraid to do anything. If the thing happens to go just right then remember that you probably didn't accomplish it all alone and entirely unaided. Maybe there were others present. A position of responsibility means an opportunity for leadership. If you haven't the quality of leadership, all the authority in the world will not confer it on you; it must be developed inside yourself.

The foregoing is really a part of the Searles Lake development story and, as Doctor Teeple says, it may be particularly useful to young men "at this time when business is so permeated with glorified office boys who call themselves executives."

We are always glad to stress fundamentals in these columns, and we believe those which Doctor Teeple has laid down are very important, not only to the younger men, but to some of those whose graduation is years behind them but who have never learned these cardinal points.

Research the Trust Buster

A FEW years ago, when reputations were made through the gentle art of compelling combinations to dissolve and reorganize their business affairs. the activity gained the name of "trust busting." In those days it had to be done through the courts, but today there are other methods, and consequently the consumer's attitude toward mergers and combinations has changed.

In discussing the control of oil production, the *Chicago Tribune* recently said editorially:

> Combinations in restraint of trade no longer hold the menace in the consumer's mind which they once had. For one thing the technological advances of the last twenty years have left only the fewest commodities for which there are no adequate substitutes available at only slightly higher prices. If a combination controlling a commodity attempts to bleed the public which must buy it by raising prices beyond reasonable levels, the probability is that a substitute commodity will seize the markets. If such a commodity is not already known, its discovery can be predicted with something amounting to certainty.

There is much in experience to substantiate this point of view. Research has become one of the greatest factors opposed to stabilization, and those who employ it to the full are the only ones who look to the future with confidence, realizing that, while tomorrow they may not be manufacturing what they do today, they will nevertheless be prominent among those present in the particular field with which they are identified.

The great corporations, if they would, could not monopolize scientific thought, and the constant increase in appreciation of the work of the scientist tends to strengthen the consumer's faith in the laboratory as a means for saving him from the pressure of any over-greedy merger, trust, or cartel.

The Value of Publication

THE satisfactory increase in the circulation of INDUSTRIAL AND ENGINEERING CHEMISTRY might be taken to indicate a growing appreciation of the publication of technical articles, particularly in the chemical field, and such is undoubtedly the case. But there is another sort of value in publication which we are reminded to stress after reading the addresses of F. B. Jewett, president of the Bell Telephone Laboratories, and of Willis R. Whitney, director of the Research Laboratories of the General Electric Company.

If the younger men of the type so necessary in industrial progress are to produce the utmost for their employers, they must be given satisfactory surroundings in which to work, ideal conditions of association with their fellows, suitable tools, and, to quote Doctor Jewett, "we must see to it that a just recognition of their achievement is accorded them." This does not mean simply an adequate monetary return, which, though necessary, sometimes ranks second in importance to the individual, who wishes his fellows to know what he has been enabled to accomplish. Now to quote Doctor Whitney: "Publication in some form to bring recognition by one's peers is the nearest equivalent to the artistic painting, the beautiful poem, the enduring sculpture, and the splendid architecture of other creators. The most altruistic and far-seeing leaders realize the importance of this encouragement and even those who have never analyzed it instinctively feel its value."

And yet in how many laboratories is this fact disregarded? Some of the nicest work in the country has progressed and is progressing under conditions which, so far as their colleagues know, leave those engaged just where they were when they accepted their employment. Many firms have not yet learned that the real difference between competitors is a difference in their ability to apply to their own production problems the data secured through research. In every piece of research there is something which can be published to advantage without disclosing those details which are properly regarded as the confidential information of the concern. And such publication is of value, not only to our profession, but to the individual worker and therefore directly to his employer. Were we to choose a slogan for Industrial and Engineering Chemistry, we would be strongly inclined toward "Share your knowledge."

Common Sense in Conservation

IN THESE days of conservation the tendency to argue from the specific to the general is illustrated by the popular notion that, no matter what we do with our natural resources, science—and particularly chemistry—will come to the rescue in ample time. We have frequently pointed out that chemistry is not a substitute for common sense, and that, while the record is a magnificent one, whatever may be done through research is no excuse for the improper management of such resources as we now have.

The burden already placed upon chemistry to turn waste organic material into humus for denuded soil indicates one field in which failure to use good judgment has allowed a mildly acute and easily corrected condition to become one that is both chronic and serious. We refer to what is taking place in some parts of the West in permitting some grazing lands to be turned into desert wastes. In that part of our country containing the higher water sheds there are vast areas unsuited for agriculture but satisfactory for timber, for grazing, or for both. If the grazing is moderate, there is direct benefit, for the grass receives a needed trimming and the fire hazard is diminished. If adequate rainfall follows soon after the grazing, Nature will restore itself even though the grazing may have been excessive. If, on the other hand, the grazing has been even slightly excessive and is followed by one of those frequent periods of drought, the very roots of some of the grass lose their vitality. If further grazing follows together with the trampling of sharp hoofs, the destruction is complete. With the vegetation gone the soil begins to move and, as semi-arid regions have torrential rains, the soil movement becomes pronounced. The high elevations are robbed of valuable soil and the lower levels which receive the silt become water-logged. This question of stream-borne silt is of grave importance in irrigated areas and consequently to the country as a whole, since nearly one-third of our agricultural lands depend to some extent upon water transported from far-away mountains to the more easily accessible lowlands.

This may be illustrated by a hypothetical case of a stream having a gradient of five feet per mile throughout a hundred-mile length. With such a fall the stream will keep its channel scoured, but if heavy accessions of silt are received the stream begins to meander. This may easily lengthen the stream to two hundred miles with a gradient of two and one-half feet per mile. The stream can keep no channel. It fills more and more. Water tables rise. Evaporation takes place at the surface. The soil becomes alkaline with salts. And now the chemist is consulted. Already the middle Rio Grande Valley has undertaken a reclamation project, not primarily to get water for irrigation but rather to get rid of seepage. The work, which will cost about ten million dollars when completed, will leave the land no more productive than it was before the erosion on the high lands started to fill the valleys. The project to correct conditions in this mile-high valley was started with the slogan, "United we drain, divided we drown."

The lack of vegetation to help regulate drainage from the highlands results in excessive cutting of stream beds, so that streams once suitable for irrigation are now so deep in their banks as to make the water unavailable except by pumping.

It will be seen, then, that the simple matter of unregulated grazing on private lands and on the vast public domain—for grazing is regulated in the national forests—contributes to a destruction of natural resources in many directions. Valuable soil is lost to the highlands and water sheds, to which it cannot be restored, silt is carried into the valleys where it presents a variety of difficulties, and the utility of some stream beds is maintained only at greatly added expense, if at all. We have here a national problem calling for the application of good judgment while the situation, though acute, may still be remedied. After ultimate destruction has taken place it is too late for even the chemist to be of service.

A New Coagulant

STRICTLY speaking, ferric chloride in solution is not a new coagulant, but for many industrial purposes its price has prohibited its use. It frequently happens that the adoption of a material for a particular large-scale use leads to its manufacture in such quantities as to bring the price within the reach of others long interested but not able to buy. It is in this connection that we note with interest a contract recently awarded the Pennsylvania Salt Manufacturing Company by the Sewerage Commission of the City of Milwaukee, calling for between 2000 and 2500 tons per year of ferric chloride in solution at a price of $2.08 per hundred pounds on the anhydrous basis, delivered at the sewage plant. The solution will be transported in rubber-lined tank cars and will replace chlorinated copperas heretofore used. The availability of ferric chloride in solution in quantities that will greatly reduce its price would seem to open up a number of possible applications and make it a direct competitor with the older coagulants. Subsequent developments should afford much of interest.

Bind a Spare Set

THE material included in the Society's publications is being found so valuable by the management and research staffs of industry, as well as by those who consult libraries, that in many places the bound volumes show appreciable wear. The librarians and research directors wonder how long these journals will last and realize that their replacement may be difficult. The publications of the Society will grow rather than diminish in value. The price today of securing and binding a spare set to be put in the archives until needed is very small. The cost of replacement in future is sure to be high if, indeed, some numbers are obtainable at all. Foresight would seem to indicate the desirability of binding a spare set.

Automatic Plating Machinery[1]

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IT IS a comparatively few years since the use of automatic plating machinery was exceptional, and the usual method was for workmen to carry the articles to be plated from tank to tank for the various operations. Today both automatic and semi-automatic handling of plating operations are common. This tendency towards automatic operation is undoubtedly due primarily to the recent demands for large quantities of plated materials, which might be more economically produced by the use of equipment which greatly lowers the labor required. Contributing factors are the development and technical control of more rapid plating methods, and the requirement on the part of purchasers of plated goods of more uniform quality of electrodeposited coatings.

This requirement usually takes the form of a specification that the plated articles shall successfully withstand the action of an accelerated corrosion test for a stated number of hours. The most widely accepted test is the salt spray test,[2] and the usual requirement for articles of steel, plated with nickel or chromium, is 15 hours, though 50 hours is specified by some large concerns. It has been shown by Baker,[3] Thomas and Blum,[4] and Baker and Pinner[5] that the protective value of electrodeposits composed of such metals as copper, nickel, and chromium depends primarily on the thickness of the deposits. Without extending this paper to review the earlier work, it may be briefly stated that if the article is finished in nickel the total thickness of the electrodeposited coating should be not less than 0.001 inch, and that it should be made up of two layers, copper and nickel, or preferably three layers, nickel, copper, and nickel. However, if the final coat is chromium, the thickness of the preliminary plating with copper and nickel may be decreased to perhaps 0.0006 inch, if the thickness of chromium is from 0.00001 to 0.00002 inch.

The relationship of labor costs, thickness of deposits, and sequence of operations to automatic plating methods will subsequently be discussed. It is desired, first, however, to indicate in a general way the considerable number of operations involved in both preparing an article for plating, and in the actual plating process. This description is not intended as an actual specification of operations to produce a particular finish or given degree of protection, but rather as an indication of the amount of labor which must be performed in plating by manual methods, and of the intricacy of the mechanism required for automatic operation.

Preparation of Articles for Plating

A great many articles go from the manufacturing process to the plating department without the necessity of any immediate preparation such as polishing, tumbling, or sand-blasting to remove scale. Other articles will require such treatment to remove heavy scale from prior manufacturing operations such as heat-treating or forging, and may also have to be polished so that a bright or lustrous finish can be secured upon at least a portion of their surface.

Polishing is usually done by means of built-up cloth wheels on the surface of which there is glued the proper abrasive. Several years ago Turkish emery was the principal abrasive used. This is still employed for some fine polishing, but at present aluminous artificial abrasives are almost exclusively used for heavy polishing. The polishing operation is divided into several steps, using first coarse abrasive and working down through various grades to the finest abrasive required. A better finish is secured from the last polishing by using a polishing grease which may be applied either to the surfaces to be polished or, less economically, to the surface of the polishing wheel. The abrasive is worn from the wheels in a few minutes or hours of operation, dependent upon the nature of the polishing operation, and the wheels are then returned to the wheel set-up room, where they are dressed or cleaned off and have another coat of abrasive glued to them. They are then dried from 8 to 48 hours, practice varying in different shops, are balanced, and are again ready for use.

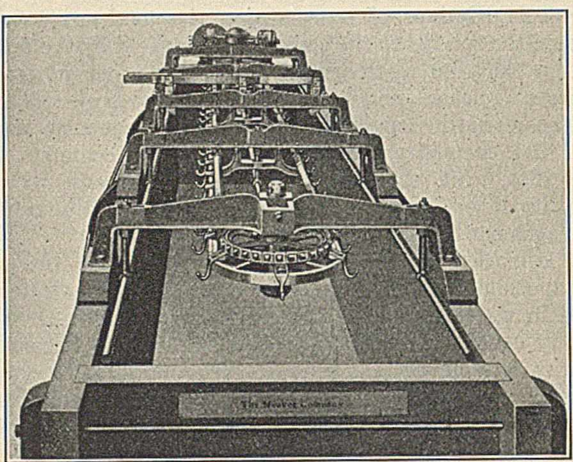

Figure 1—Semi-Automatic Plating Tank
Loading end in foreground. Variable-speed driving mechanism for conveyor in background.

After the articles enter the plating room they are usually placed on plating racks for the series of operations which are to follow. These operations will depend upon the base metal and of course upon the plate that is to be applied. If the articles are of steel and are to be finished as nickel-plated articles, the sequence of operations will be somewhat as indicated below.

(1) Clean in an alkaline cleaning solution.
(2) Rinse with water and scrub with finely powdered pumice if necessary.
(3) Rinse with water.
(4) Dip in dilute hydrochloric or sulfuric acid (about 2 *N*) to remove the film of oxide on the metal.
(5) Rinse in water.
(6) Plate in a nickel-plating solution.
(7) Rinse in water.
(8) Plate in an acid copper-plating solution.
(9) Rinse in water.
(10) Plate in a nickel-plating solution.
(11) Rinse in cold water.
(12) Rinse in hot water so that the articles will dry quickly upon being removed from the rinse.

The next operation, if a lustrous surface is desired, is to buff the polished surfaces to bring out the required luster.

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[1] Received March 11, 1929.

[2] See Bur. Standards, *Circ.* **80**, or Rawdon, "Protective Metallic Coatings," Chemical Catalog Co., 1928.

[3] Baker, *J. Soc. Automotive Eng.*, **14**, 127 (1924).

[4] Thomas and Blum, *Trans. Am. Electrochem. Soc.*, **48**, 69 (1925); **51**, 271 (1927).

[5] Baker and Pinner, *J. Soc. Automotive Eng.*, **22**, 231 (1928); see also *Trans. Am. Electrochem. Soc.*, **54**, 337 (1928).

In place of the above sequence of operations, the first nickel plating may be omitted and plating with copper from a cyanide copper solution substituted. In that case the plating with copper from the acid copper solution may also be omitted. In either case the articles may be buffed after copper plating, and then racked and returned to the plating room for the final nickel plate. If the article is to be plated with zinc or cadmium, the cleaning operations will be somewhat as above, but the plating operations will be entirely different.

Manual Plating Equipment

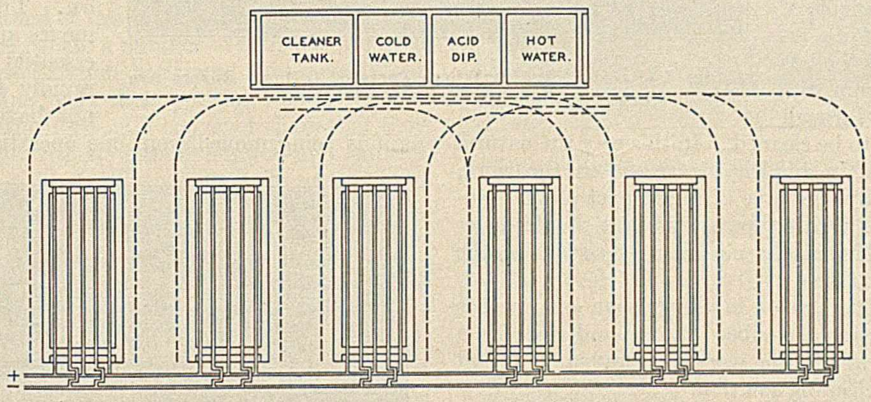
In the older books and articles dealing with plating one will find descriptions almost exclusively of plants in which the various tanks are arranged so that the operator carries the work by hand from one tank to the next. Today such plants are for the most part in operation only when the total volume of work to be plated per day is small.

Semi-Automatic Plating Equipment

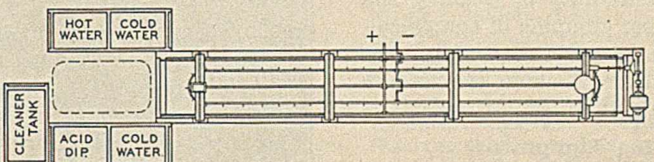
Perhaps the first step in the evolution of automatic plating and methods was the substitution of what is known as "semi-automatic" plating tanks for the older "still" plating tanks. These tanks are furnished by practically all manufacturers of plating equipment, are alike as regards operation, and differ only in mechanical details. Such a plating tank is shown in Figure 1. It is substantially an ordinary plating tank equipped with a chain conveyor so that the operator can hang the work to be plated on the chain at one end of the tank, after which it will travel slowly down the tank between two rows of anodes, around a sprocket at the far end of the tank, and again travel slowly to the operator. It is apparent that this arrangement will save something in labor, because the operator can load and unload the entire tank at a single point, and save the time of walking back and forth with work.

Figure 2 shows diagrammatic layouts which might be used in plants equipped, respectively, with still-plating tanks and a semi-automatic plating tank for nickel plating. In this diagram there is indicated the difference in labor required to keep the numerous small tanks operating as compared with the one larger semi-automatic tank. This, however, is only one of a number of advantages possessed by this equipment. While the motion of the work through the solution is relatively slow, it is sufficient to avoid to some degree the settling of the sediment from the solution upon the upper surfaces of the work. Fine particles of sediment settling on the work in this way result in a rough surface, often incorrectly characterized as a burnt deposit. It will be difficult or impossible to buff this deposit, and even if the buffing can be accomplished the deposit will be relatively porous and of poor protective value. The slight motion of the work in the solution also tends to sweep away gas bubbles which would otherwise form and remain at single points, resulting in pitted deposits.

Moreover, some anodes may project out into the solution farther than others, and in other cases anodes which may appear to be in good condition, as viewed from the top of the tank, may actually have become very small under the solution and may consequently give a low current density to work opposite them. If the work is stationary, anodes which are too close will give rough or burnt deposits, while anodes which are under-sized or farther away will give a deposit thinner than the average. When the work is moved in succession past all such anodes, every piece of work in turn is subjected to the same conditions. It is not exposed to anodes which would tend to give a burnt deposit long enough for this condition to become serious, nor is any one piece underplated because of being continuously opposite anodes which give low current density. Furthermore, if the operator places the work in the ordinary plating tank and later withdraws it, there is no assurance that the time of plating will be the same on all articles. Since with other conditions such as current density fixed, the time of plating directly determines the thickness of plate, and a uniform time of plating is essential. If the articles are loaded into one end of a semi-automatic plating tank, they will, of course, be plated for just the amount of time that is required for the conveyor to move them from that position throughout the entire length of the tank and back again. Although the speed of the conveyor is variable and subject to adjustment, it is comparatively easy to assure a uniform time of plating. Under these conditions, too, the plating tank is ordinarily filled with work, except at the beginning and close of the day when the tank is started up and shut down. It is therefore possible to maintain a steady or uniform current on the tank, and this means a more or less uniform current density for each type of article, although articles of different configuration may receive different current densities. To summarize, then, semi-automatic tanks possess an advantage over simple plating tanks in that they should and do give more uniform plating conditions and lower percentages of rejections.



TYPICAL LAY-OUT OF HAND TANK PLATING PLANT



SEMI-AUTOMATIC EQUIPMENT.

Figure 2—Diagrammatic Layout of Two Plants of Equal Capacity, One with Manually Operated Plating Tanks and the Other with a Semi-Automatic Plating Tank, Illustrating Difference in Required Labor

In this connection it should perhaps be mentioned that the cathode or work rods on some plating tanks are fitted with equipment to give them an oscillating motion, either longitudinally or vertically in the tank. This motion will cause a movement of work past the solution and therefore possess some of the advantages of the semi-automatic tank. It is apparent, however, that the two are not equivalent. Such oscillating equipment has one special advantage in certain cases in that the

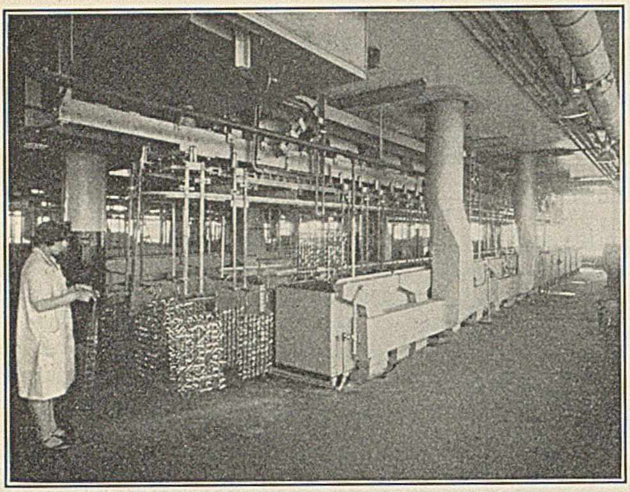


Figure 3—Full Automatic Conveyor Used for Nickel-Plating Safety Razors, Showing Loading and Unloading Ends

movement can be made relatively rapid so that the agitation is more effective than in the continuous or semi-automatic tank.

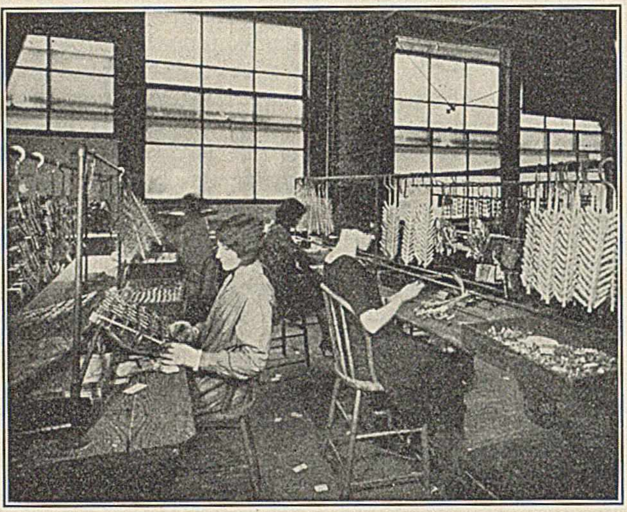


Figure 4—Racking Tables Where Parts of Gillette Razors Are Placed on Racks for Plating

Along with the semi-automatic plating tank, washing machines have come into use. These machines as a class are alike in principle but may differ considerably in regard to construction. In their essentials these washers consist of a housing through which the work is passed either on racks hung on a conveyor or on a simple apron conveyor. The bottom of the housing contains a tank which holds the cleaning solution. This is heated either with closed steam coils or by the direct injection of live steam. Pumps capable of handling a large volume of solution at low heads draw the hot cleaning solution from the tank and discharge it through nozzles onto the work to be cleaned. In this way the natural action of the solution, in emulsifying grease on the work, is greatly augmented by the force of the impact of the solution. When machines of this type are used, it should never be necessary to supplement the cleaning by scrubbing the work with powdered pumice.

It is usual to have two zones in the washer, one for the actual cleaning operation described above, and one for a similar operation in which the work is sprayed with hot water to rinse off the cleaning solution.

A combination of a continuous washer and a number of semi-automatic plating tanks, together with a few ordinary tanks for dip or rinse operations, will do much to lower the labor cost, and also to assure uniformity of cleaning and uniformity of plating. By a proper grouping of equipment, operators should be able to handle the work through the process without being required to walk more than a few steps between successive operations.

Full Automatic Plating Equipment

"Full automatic" plating equipment refers to equipment in which the transfer of work between operations is all done by machinery. It is merely necessary for the operators to place the work to be plated on racks on a conveyor at the loading end of the equipment and remove it after plating and final rinsing from the discharging end. Here again all the equipment is alike in principle and the differences are found in the methods of transferring work between operations and in carrying it through the tanks in which the operations take place. The arrangement may be such that the equipment is in one continuous line, the work entering at one end and being discharged at the other. In other cases the work may move away from the operator in one row of tanks, make a U turn, and return through a second line of tanks placed parallel to the first. The charging and discharging ends are thus brought close to each other.

Such an arrangement in use for the plating of the safety razors by Gillette Razor Company is shown in Figure 3. The particular conveyor shown is the overhead type manufactured by the Hanson-Van Winkle-Munning Company. The parts to be plated are placed on the plating racks on racking-up tables, as are shown in Figure 4. These are hung on the carriers, which are shown in Figure 3. The carriers in turn are conveyed in a horizontal direction by a conveyor chain similar in many respects to that of the semi-automatic equipment. In the upper central portion of Figure 3 is shown a cam device which is synchronized with the conveyor chain. When one of the rack carriers reaches the proper point, it is picked up by this cam device, raised almost vertically, carried forward at a higher level, and lowered onto the conveyor chain at a point somewhat ahead of that from which it was picked up. In this way the work is moved, for example, from the loading end into the first tank of the series. In like fashion other cams or "transfers" remove the work from this tank and place it in the next, and so on. The conveyor chain moves quite slowly, but it is essential that the transfer act rapidly so that the work will not have a chance to dry off as it is being moved from one operation to the next. The

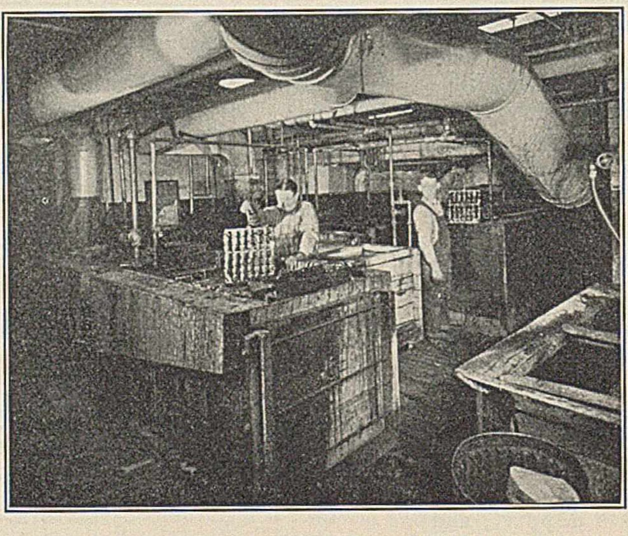


Figure 5—Old Manually Operated Plating Tanks Used in Plating Gillette Safety Razors

Gillette plant has three of these full automatic conveyors which are used, respectively, for nickel plating, silver plating, and gold plating. The gold plating plant is the largest of its class in the world. It now is plating approximately 50,000 razors per day and is capable of doing 50 per cent more. The installation of this equipment has reduced the amount of labor to approximately 10 per cent of that used with still-plating tanks. A part of the old plating plant, which was in use before the installation of the automatic equipment, is shown in Figure 5, and the difference in the two installations is most striking.

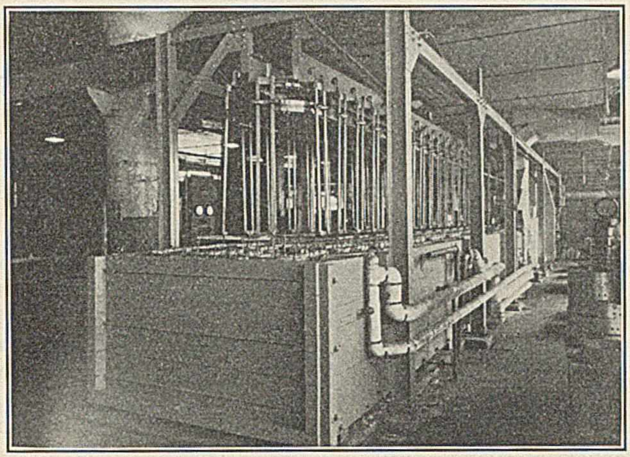


Figure 6—Full Automatic Conveyor Used for Plating Meter Bases

Another full automatic plating tank of the same type and make, which is in use at the Fort Wayne Works of the General Electric Company for the plating of meter bases, is shown in Figure 6. This photograph illustrates particularly well the U turn at the end of the automatic conveyor opposite the loading and unloading end.

Figure 7 illustrates the type of full automatic plating equipment manufactured by the U. S. Galvanizing and Plating Equipment Corporation. The material to be plated enters on racks at the near end and these are unloaded from the far end. The method of transfer is illustrated at the left-hand side of the figure, where a number of transfers are used in sequence without intermediate horizontal movement. The arms shown rotate, and have their position and movement so synchronized with the horizontal conveyor chain that they may pick up one of the cathode bars illustrated and transfer it, together with the work hung upon it, from one tank to the next.

Figure 8 shows the discharge end of another "straight-away" full automatic plating plant. In this machine transfer from tank to tank is accomplished by arms, actuated by large cams, which pick up the cathode bars and attached work, raising these from one tank, moving them forward, and setting them down in the next tank, the cathode bars again being in position to be carried forward by the conveyor chains on both sides of the equipment.

The cathode bars, after removal of the radiator shells, are carried by the conveyor chain under the tanks back to the loading end. This equipment was manufactured by the Mitchell Engineering Corporation, and is in use by the Pontiac-Oakland Motor Car Corporation. The sequence of operations is as follows: The shells are washed, before and after polishing, in a power washer through which they are conveyed on a separate mechanism. The operator then hangs the shells, three in a row, on the conveyor of the automatic plating machine. They pass in turn through an electrolytic cleaning operation, a water rinse, a sodium cyanide dip, a cyanide copper "strike," where they are plated for a moment at high current density, a cyanide copper-plating tank, a rinse, a nickel-plating tank, a cold-water rinse, and a hot-water rinse. The shells are subsequently buffed and chromium plated.

In another type of full automatic equipment, manufactured by the Meaker Company, transfer of cathode bars and work from tank to tank is by means of chains instead of cams.

Application of Different Types of Plating Equipment

Full automatic plating equipment has all the advantages of the semi-automatic equipment plus a further saving in labor and an assured fixed time for each operation involved in the sequence. The time in any operation is determined by the speed of the conveyor and by the length of the tank in which the operation is carried out. Since the conveyor is equipped with a variable-speed drive, it is possible to regulate the time of an operation. This, however, necessarily varies the time of all other operations in proportion. This has its advantages and disadvantages. It requires that the scheme of plating be thoroughly worked out in the first place, but after that is done the equipment assures that operators cannot over-time some operations and under-time others. On the other hand, should changing circumstances require a modification of the ratio of the time for one operation to that for another, this variation can only be obtained by changing the lengths of those units requiring a different ratio of time and this means rearranging much of the equipment.

It is apparent that equipment for automatic plating involves a greater investment, and it is upon this question of investment and labor savings that the decision of the type of equipment to be installed will usually depend. Phillips and MacCauley,[6] in discussing the full automatic plating equipment shown in Figure 8, give the following comparison, based on the copper plating and nickel plating of 1500 Pontiac radiator shells per day:

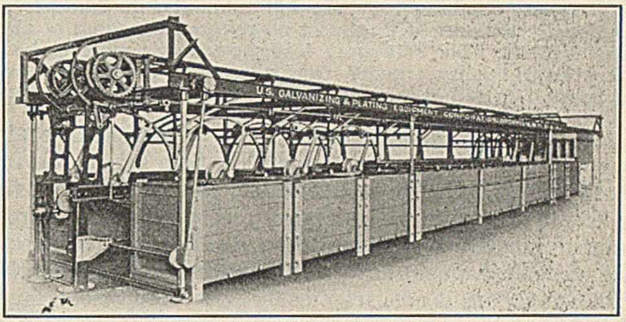


Figure 7—Full Automatic Conveyor Used for Zinc Plating Meter Bases

KIND OF EQUIPMENT	FLOOR SPACE REQUIRED	NUMBER OF MEN
	Square feet	
Manually operated tanks	7902	18
Semi-automatic machines	1634	9
Full-automatic machines	1040	2

Continuing further, they state:

> When the cost of handling and trucking the radiator shells between buffing operations and the actual buffing costs are taken into consideration, the saving made in favor of the full-automatic machines is much greater.
>
> With the manually operated tanks, the quality of plate was variable, with an exceptionally high number of rejections due to burns, digs, and scratches. The salt-spray test indicated that the thickness of no two plates was the same, and, under test, failure resulted in from 5 to 10 hours.

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[6] Phillips and MacCauley, Annual Meeting, Society of Automotive Engineers, January, 1929.

The semi-automatic machines produced much more uniform plate and rejections were reduced at least 10 per cent as compared with the product of the manually operated tanks; but there was still a large rejection on account of scratches, burns, and digs from handling and scrubbing. The salt-spray test indicated that many spots were breaking down where the copper plating had been cut through in the buffing operation, with only a thin nickel plate over parts of the steel. Where the copper plating had been cut through, the nickel had a tendency to be gray and the buffer naturally put more pressure at these spots to get the color on the nickel; the resulting plate was therefore very thin. The salt-spray test, however, indicated a plate much superior to that produced in manually operated tanks; under test, the plating lasted 10 to 12 hours.

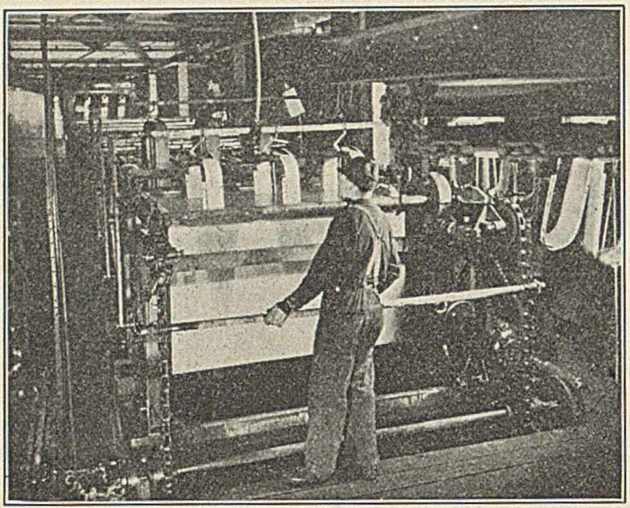

Figure 8—Discharge End of Full Automatic Conveyor Used for Nickel Plating Pontiac Radiator Shells

The plate resulting from the full automatic machines is exceptionally uniform, with almost no rejections because of plate imperfections. The salt-spray test showed this plate to be of exceptional quality; under test, the plate lasted well over 15 hours.

On the basis of labor-saving alone the full automatic equipment would have paid for itself in less than a year. If full credit were given for reduced rejection, cost of rework, and the indefinite but nevertheless material benefits resulting from assured production and improved quality, it is seen that the equipment would have paid for itself in a few months. This comparison is not exceptional; rather it represents fairly well the average case where a large volume of the same class of work is to be plated.

In a particular case it is not difficult to compile predetermined costs if the sequence of operations and the time for each have been definitely set. The equipment which will prove most economical in operation can then be selected.

It is possible to make a few general statements. Still-plating tanks are justified only if the volume of work is small or if the plating time is extremely short. Semi-automatic tanks cost only a small percentage more, if the comparison is made on the basis of the completed installation, including generators, and semi-automatic operation usually will eliminate at least 50 per cent of the labor required for still tanks.

Full automatic equipment has its application in the plant of the large manufacturer. It is usually not suitable for even a large-sized job plating plant, and in some instances the articles to be plated may be of such size and shape that they cannot be well handled in automatic plating equipment, even though it is otherwise ideal.

Installation of full automatic equipment requires prior painstaking investigation of all problems likely to arise in operation: solutions for and time of cleaning and rinsing, sequence of actual plating operations, time of plating, solutions for plating, permissible current densities, tendencies toward burned or pitted deposits with the methods of racking that must be used if the installation is adopted, and so on. Contemplated full automatic installations should be passed on by competent electrochemical, electrical, and mechanical engineers, to eliminate all hit-and-miss guess work. If, however, the process is sufficiently worked out in advance, and is adaptable to full automatic equipment, it has the advantage of: (1) saving labor, eliminating up to 90 per cent of that required for hand methods; (2) insuring more nearly uniform quality than can be had by other methods; (3) reducing required size of generating equipment, since this can be continuously kept under full load, with resultant elimination of peak or overload capacity otherwise required to compensate for idle time involved in manual methods; (4) reduction of percentage of work rejected, and (5) predetermined productive capacity for a fixed working period. However, unless the production is reasonably uniform and of sufficient volume to warrant the larger investment required for full automatic equipment, the latter may prove an expense rather than an economy.

Acknowledgment

The author acknowledges his obligations to the several concerns mentioned in the paper for illustrations, and data on installations.

Record Production of Dyes in 1928

Preliminary figures compiled by the United States Tariff Commission show that the domestic production of coal-tar dyes for the calendar year 1928 exceeded that for 1927 by approximately 1,400,000 pounds. In 1928 production by forty-seven firms of approximately 96,600,000 pounds was an increase of 1.5 per cent over the production in 1927. Sales in 1927 were 93,300,000 pounds, valued at $39,790,000.

The outstanding features of American dye production in 1928 were increase in production of vat and other fast dyes, production of many new vat and specialty dyes, reduction in the number of domestic manufacturers from fifty-five to forty-seven, increase in unit price of sales of all dyes, in exports, and in dye imports.

The production of fast dyes in 1928 established a new record with a total of more than 6,300,000 pounds as compared with 5,961,688 pounds in 1927. This increased consumption of vat dyes indicates the growing realization by the public that, although the fast dye is more expensive, the cost of dye per yard of fabric or per garment is, in general, but a small fraction of the total cost and that it is far more economical to invest in fast-dyed fabrics or garments.

Domestic Production and Sales of Coal-Tar Dyes

YEAR	PRODUCTION	SALES	
	Quantity	Quantity	Value
	Pounds	*Pounds*	
1914	6,619,729	....	....
1920	88,263,776	....	....
1921	39,008,690	47,513,762	$39,283,956
1922	64,632,187	69,107,105	41,463,790
1923	93,667,524	86,567,446	47,223,161
1924	68,679,000	64,961,433	35,012,400
1925	86,345,438	79,303,451	37,468,332
1926	87,978,624	86,255,836	36,312,648
1927	95,167,905	98,339,204	38,532,795
1928	96,625,000	93,302,000	39,790,000

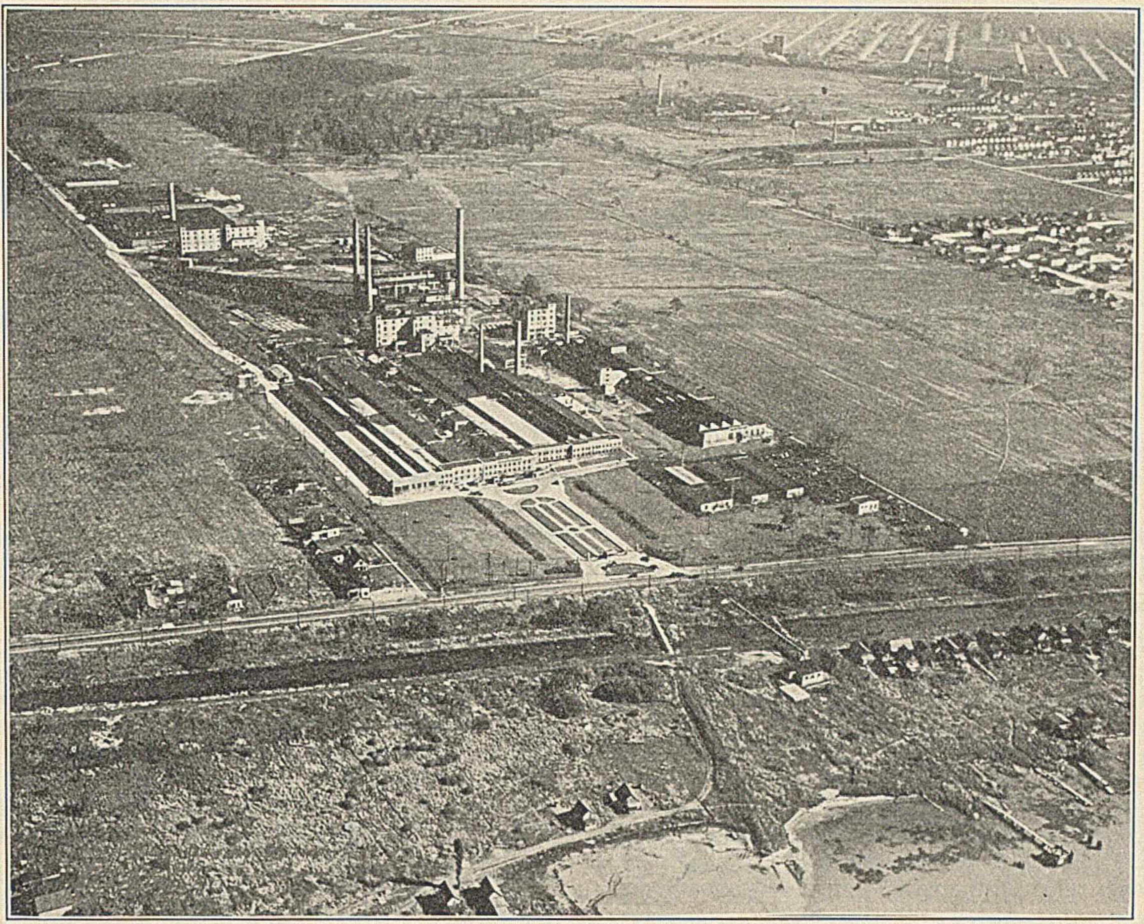

Figure 1—Plants of the Du Pont Cellophane and Du Pont Rayon Companies at Buffalo, New York

Manufacture and Properties of Regenerated Cellulose Films[1]

William L. Hyden

Technical Department, Du Pont Cellophane Company, Inc., Buffalo, N. Y.

THE commercial production of films of regenerated cellulose in sheet form, such as Cellophane, has been steadily increasing during the past few years. Cellophane is used chiefly as a wrapping material. Being transparent, lustrous, durable, flexible, and impervious to air, grease, germs, and dirt, it makes a highly protective as well as an artistic wrap.

Note—"Cellophane" ("cello," cellulose; "phane," glass) is the registered trade-mark of the Du Pont Cellophane Company, Inc., used to designate its transparent cellulose sheets and films. Similar films are manufactured by several European corporations.

The raw material for Cellophane is cellulose in the form of purified wood or cotton pulp sheets. By the viscose[2] process these pulp sheets are put into colloidal solution and the cellulose is regenerated into continuous transparent films.

History

Although Beadle[3] and others prepared cellulose films experimentally, the industry of manufacturing transparent films of regenerated cellulose was founded by Brandenberger,[4] of Neuilly sur Seine, France, in 1908. Brandenberger first specialized in the chemistry of dyeing, printing, and finishing of cotton cloth. He believed that the beauty of cotton fabrics could be greatly enhanced if they could be given a luster like that of silk. He attempted to achieve this result by applying viscose, at that time a new cellulose solution, to the cloth and by imprinting the viscose he hoped to impart lustrous designs to the fabric. The first experiments of this nature were unsuccessful. Although the cloth had increased luster, it was too stiff and entirely unfit for garment or other use. He then conceived the idea of making a thin, lustrous cellulose film separately and afterward applying it to the cloth. His effort to produce the cellulose films separately led to the idea of their commercial manufacture.

The first machine for the continuous manufacture of transparent films was designed and built by Brandenberger at the Blanchisserie et Teinturerie de Thaon-les-Vosges, France, in 1908. The product of this machine was thick and brittle and was not very useful. By 1912, however, Brandenberger had succeeded in producing thin, supple films comparing in thick-

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[1] Received March 13, 1929.

[2] Cross, Bevan, and Beadle first described the preparation of viscose, *Ber.*, **26**, 1090, 2524 (1893).

[3] Margosches, "Die Viskose," p. 79, Klepzig, 1906.

[4] Brandenberger, U. S. Patents 981,368 (January 10, 1911) and 1,601,289 (September 28, 1926).

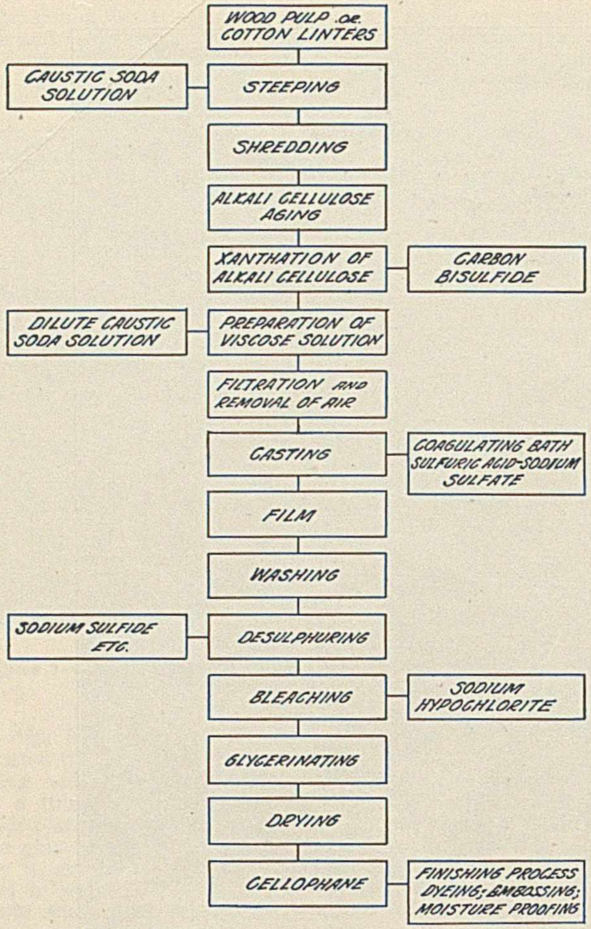


Figure 2—Flow Sheet for Production of Cellophane from Wood or Linter Pulp by Viscose Process

ness with the lighter weight present-day Cellophane (approximately 0.02 mm.). This development resulted in the production of a salable film. Numerous other improvements have since been made and the applications of Cellophane are constantly increasing.

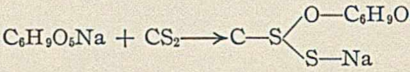
Manufacture

For the preparation of Cellophane it is essential to use purified wood or cotton pulps. Although transparent films of regenerated cellulose have been made from cuprammonium solutions[5] of cellulose, the viscose process has proved more adaptable and economical for commercial use.

The flow sheet for the manufacture of Cellophane by the viscose process[6] is given in Figure 2. Bleached pulp in rectangular sheets of from 80 to 90 per cent alpha-cellulose content are placed in steeping presses into which is introduced an 18 to 20 per cent sodium hydroxide solution. The temperature is maintained constant during the soaking process. During this treatment the fibers swell and form a rather unstable alkali-cellulose compound and at the same time the hemicelluloses dissolve in the caustic. The excess sodium hydroxide solution, containing the dissolved hemicelluloses, is pressed out until the weight of the pressed alkali-cellulose sheets is about three times that of the dry pulp.

The alkali-cellulose is shredded into a fluffy amorphous state by machines illustrated in Figure 3. Since the viscosity of the viscose depends upon the aging time, the alkali-cellulose is stored in covered containers for a period of time at a carefully controlled temperature. The alkali-cellulose aging time and temperature have a marked effect upon the viscose viscosity (Figure 4).

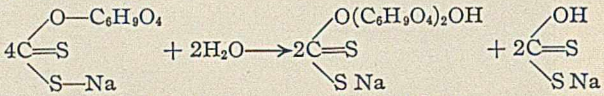
The aged alkali-cellulose is next converted into an ester, cellulose xanthate, by the action of carbon disulfide. The reaction is carried on in double-walled, tightly closed, rotating barrel-like containers (Figure 5). During the interaction the white alkali-cellulose is converted into orange-red cellulose xanthate.



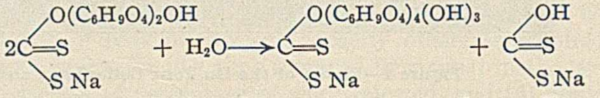
$$C_6H_9O_5Na + CS_2 \longrightarrow C{-}S\begin{array}{l}\diagup O{-}C_6H_9O_4\\ \diagdown S{-}Na\end{array}$$

The temperature, concentrations, and time are controlled factors in xanthation. Cellulose xanthate readily forms colloidal solutions in dilute caustic soda.

The freshly prepared xanthate is mixed with dilute sodium hydroxide solution until a uniform colloidal solution, known as viscose, is formed (Figure 6). As in the manufacture of rayon, before the viscose can be successfully coagulated and regenerated, it must be "ripened." During ripening, which is conducted at a constant temperature (usually in the range of 15° to 25° C.), a series of complex reactions occur which are not fully understood, despite the fact that many investigators have studied the process. It is known that the molecule becomes more complex and that the ratio of sodium and sulfur to cellulose changes. Reactions occurring during the ripening of viscose may be represented by the following equations:[7]

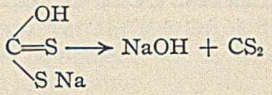


$$4\,\underset{\diagdown S{-}Na}{\overset{\diagup O{-}C_6H_9O_4}{C{=}S}} + 2H_2O \longrightarrow 2\,\underset{\diagdown S\,Na}{\overset{\diagup O(C_6H_9O_4)_2OH}{C{=}S}} + 2\,\underset{\diagdown S\,Na}{\overset{\diagup OH}{C{=}S}} \qquad (A)$$



$$2\,\underset{\diagdown S\,Na}{\overset{\diagup O(C_6H_9O_4)_2OH}{C{=}S}} + H_2O \longrightarrow \underset{\diagdown S\,Na}{\overset{\diagup O(C_6H_9O_4)_4(OH)_3}{C{=}S}} + \underset{\diagdown S\,Na}{\overset{\diagup OH}{C{=}S}} \qquad (B)$$

At the same time side reactions proceed according to the equations:



$$\underset{\diagdown S\,Na}{\overset{\diagup OH}{C{=}S}} \longrightarrow NaOH + CS_2 \qquad (C)$$

$$2CS_2 + 4NaOH \longrightarrow Na_2CO_3 + Na_2CS_3 + H_2S + H_2O \qquad (D)$$

$$Na_2CS_3 + 3H_2O \longrightarrow Na_2CO_3 + 3H_2S \qquad (E)$$

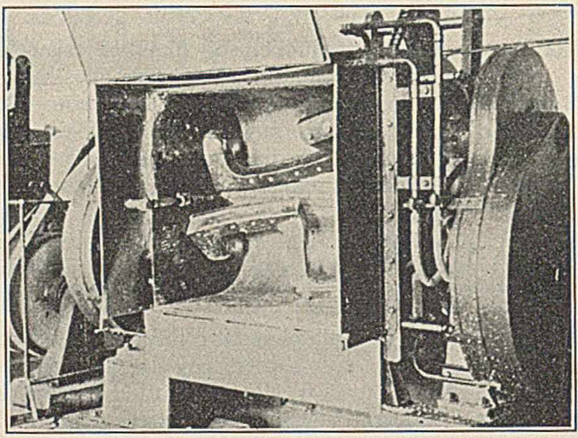


Figure 3—Shredders

While ripening, the viscose is filtered several times to remove dirt, fibers, and other foreign matter. The state of ripening is closely followed by determining the "salt number" by a method somewhat similar to the one first published by

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[5] Zeith and Ziegler, U. S. Patents 1,590,601 and 1,590,602 (June 29, 1926).

[6] For description of the manufacture of viscose see Margosches, "Die Viskose," Klepzig, Leipzig, 1906; Avram, "The Rayon Industry," D. Van Nostrand Co., New York, 1927; Hottenroth, "Die Kuntseide," S. Hirzel, Leipzig, 1926; Heuser, "Cellulose Chemistry," McGraw-Hill Book Co., New York, 1924.

[7] Heuser, "Cellulose Chemistry," p. 66.

Hottenroth[8]—namely, the determination of the concentration of a sodium chloride solution necessary to start coagulation of small quantities of viscose solution. When the desired state of coagulability is reached, the viscose is cast. To insure the production of a uniform film, free from gas bubbles, all incorporated gases are removed from the viscose by vacuum just prior to its transfer to the casting machines.

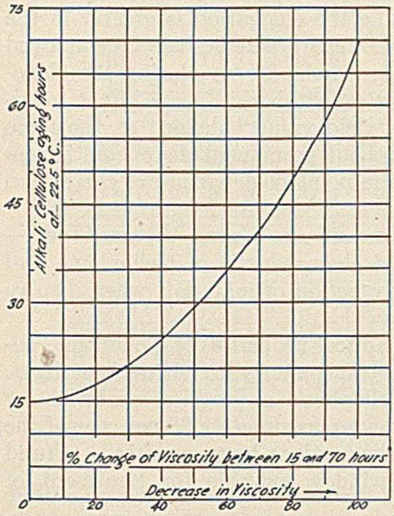

Figure 4—Change in Viscosity of Viscoses Prepared from the Same Alkali-Cellulose Aged from 15 to 70 Hours

Casting Viscose into Films

Numerous patents have been issued and methods described for the mechanism of producing continuous films of regenerated cellulose from viscose. In all methods viscose under pressure is forced to the casting apparatus, commonly called a hopper. One type of hopper illustrated in Figure 7 is equipped with non-corroding, smooth-surfaced lips (2 and 2′) which are accurately adjusted by the mechanism (3, 4, 5, 6, 7, 8) to control the dimensions of the aperture (11). A uniform sheet of viscose is extruded between the lips into a coagulating bath (usually sulfuric acid and salts), where the cellulose xanthate solution is regenerated into a cellulose film.

A second means of casting continuous films is illustrated by Figure 8. A hopper (3, 4) of fixed clearance is suspended directly above a rotating roll (5), which is partially submerged in a coagulating bath. Viscose is extruded upon the smooth surface of the moving roll, which is continuously moistened by a film of coagulating bath. The viscose is transferred in uniform thickness to the bath and, after being regenerated into a film of cellulose, is stripped from the roll (5), since the film is led over rolls (8 and 9). Figure 9 illustrates a modification of Figure 8. In this case the viscose is laid in uniform layers from the hopper (15) upon a continuous smooth belt (11) instead of a roll. As the belt moves around the partially submerged rolls (12 and 13) a long supported bath travel is afforded the film. It is stripped from the belt by being led over roll (18) and transferred to the succeeding tank by the following roll (19).

As shown in the diagrammatic sketch of the casting machine (Figure 10), after the regenerated cellulose film is formed in tanks 1, 2, and 3, it is transferred by rolls into succeeding tanks filled with fresh warm water, which removes the residual acid in the film carried over from the casting tank. The film is next passed through a solution (commonly NaOH, Na_2S, or Na_2SO_3) for the purpose of removing the sulfur deposited in the film by the decomposition of the cellulose xanthate. The film is further washed and bleached, using sodium hypochlorite. Finally it is passed through a solution of glycerol of high purity.

Because of its hygroscopicity, glycerol, which is adsorbed and tenaciously retained by the film, imparts softness and pliability. The film at this stage is completely formed and is dried by passing it over heated rolls, the desired temperature being maintained by automatic control. As the film proceeds through the drier, it comes in contact with drafts of warm air. Finally, the Cellophane is wound on cores into rolls of any desired weight.

Finishing Processes

Cellophane from the casting machine is cut into sheets approximately one meter square. Each sheet is carefully inspected and if any sheet contains imperfections, or is of low transparency, it is rejected.

Dyeing and Embossing—Cellophane may be dyed any desired color with either mordant dyes or direct colors (Figure 11). When dyed with direct colors, the operation consists merely of passing wet film through a dye bath of the correct concentration and temperature to produce the shade of color wanted. After suitable washing, the film is passed through a glycerol solution and dried. When mordant dyes are used additional baths are required, but it is possible to obtain shades of color which cannot be duplicated with direct dyes.

Cellophane can be embossed by pressure rolls or stamps of desired designs. Finishes similar in appearance to "linen" cloth, "morocco" leather, silk fabric, and other embossed patterns are possible.

Moistureproof Cellophane—Moistureproof Cellophane, which has been recently developed in America, is lustrous and highly transparent. The following table is a comparison of the moistureproof quality of this Cellophane and samples of waxed papers. The moistureproof quality is determined by sealing a piece of the material to be tested over a glass dish containing water and determining the loss in weight when the test dish is placed in an air oven at 100° F. The air in the oven is circulated by a fan and desiccated by concentrated sulfuric acid kept in flat trays. By carrying out the test at 100° F. the rate of diffusion is much greater than at lower temperatures and the test is thus accelerated.

Materials	Diffusion of Water Vapor at 100° F. *Mg. per sq. m. per hour*
Moistureproof Cellophane	270
Waxed brown paper[a]	400
Waxed glassine paper[a]	530
Average of fifteen waxed papers	22,200

[a] Represents highest quality waxed papers which have been tested.

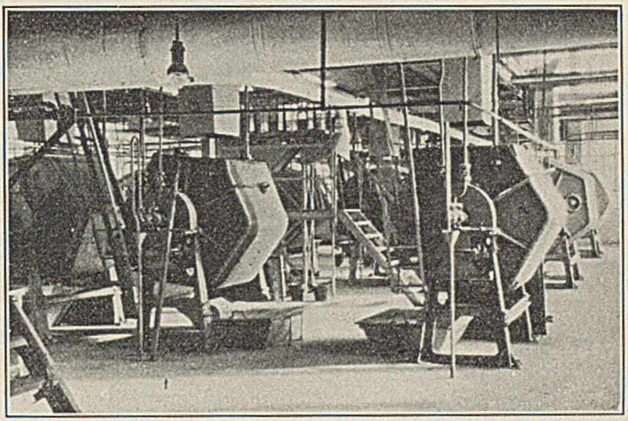

Figure 5—Rotating Barrels in Which Alkali-Cellulose Is Converted into Cellulose Xanthate by Carbon Disulfide

Moistureproof Cellophane is particularly desirable as a wrapper for food products which lose or absorb moisture when exposed to the atmosphere. As an illustration, a test made by sealing 40 grams of soda-cracker biscuits in a large paper envelope and exposed at 70° F. and 70 per cent relative humidity for 48 hours showed a gain in weight of 3.1 grams. A similar test using Moistureproof Cellophane showed a gain of only 2.0 grams after 6.5 months' exposure.

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

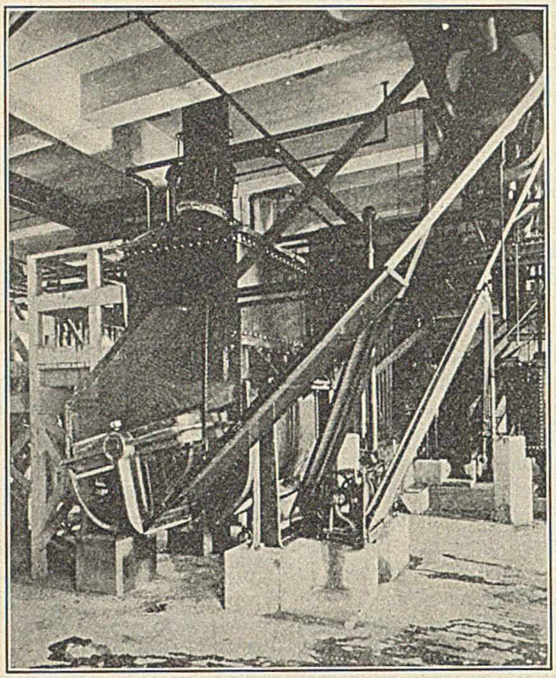

Figure 6—Mixing Room Where Cellulose Xanthate Is Mixed with Caustic Soda Solution to Form Viscose

The character of the surface of Moistureproof Cellophane is such that ordinary glues and adhesives cannot be used for sealing it and an entirely new type of adhesives has been developed to fill this need.

Physical Properties of Cellophane

TENSILE STRENGTH AND ELONGATION—Three weights of Cellophane, 33, 45, and 60 grams per square meter, are regularly produced. These vary in thickness from approximately 0.001 to approximately 0.002 inch. When thicker sheets are desired, they are made by plying together several thinner sheets using suitable gelatin or dextrin adhesives.

The tensile strength of Cellophane and some papers as measured at 60 per cent relative humidity and 70° F. by the Scott machine and Mullen tester are compared in the following table:

MATERIAL	THICKNESS	WEIGHT REQUIRED TO BREAK $1^5/_8$-INCH STRIP (SCOTT MACHINE) Longitudinal direction	Transverse direction	BURSTING STRENGTH (MULLEN TESTER)
	Inch	*Lbs.*	*Lbs.*	*Lbs. per sq. in.*
Cellophane	0.00098	15.7	7.3	26.9
Cellophane	0.00141	19.7	8.8	33.8
Cellophane	0.00193	26.8	13.2	42.1
Sulfite paper	0.00162	13.7	7.7	6.1
All-rag high-grade paper	0.00212	22.5	14.5	21.6
Sulfite bond paper	0.00296	43.0	23.2	24.9
Extra high-grade paper	0.00412	73.1	55.5	84.4

It will be observed that strength does not increase in direct ratio to increased thickness. To make comparisons of the strengths of Cellophane and other materials it is desirable to reduce the values to a unit thickness basis; usually such comparisons are made on thicknesses of 0.001 inch.

The serviceability of Cellophane is enhanced by its elastic properties. Figure 12 exhibits the relation of tenacity, elongation, yield values, and force in pounds.

From the above data it is noted that to define the physical properties of Cellophane it is necessary to designate the values in both the longitudinal and transverse directions, just as in paper description one must specify whether the quantity is measured with or against "the grain." The longitudinal direction may be defined as the dimension parallel to the forward movement of the film through the casting machine. The transverse direction is perpendicular to the longitudinal direction.

It wlll also be seen that the tensile strength is greater in the longitudinal direction while the elongation is greater in the transverse direction. These characteristics can be employed to advantage in wrapping articles by so placing the Cellophane sheet that the greatest strain will come in the longitudinal direction. The "yield value," defined as the force which may be applied without permanent distortion, is represented graphically by the point of departure of the curves from the abscissa.

TRANSPARENCY TO ORDINARY AND ULTRA-VIOLET LIGHT—Transparency is the chief characteristic of Cellophane and permits its use for the protection of materials when display is desired.

One of the interesting optical properties of Cellophane described by Pfund[9] is its transparency to ultra-violet light. This property makes Cellophane a practical material for windows,[10] which will allow approximately 70 per cent of the shortest waves reaching the earth to be transmitted. Pfund describes a Cellophane window suitable for treatment of

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[9] Pfund, Johns Hopkins Hospital, *Bull.* **40,** 228 (April, 1927).

[10] Pfund, *J. Am. Med. Assocn.*, **91,** 18 (1928).

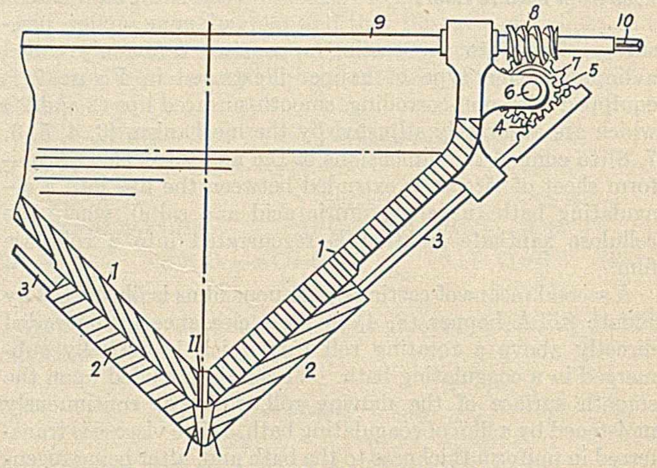

Figure 7—Hopper Used for Casting Viscose
(British Patent 3929)

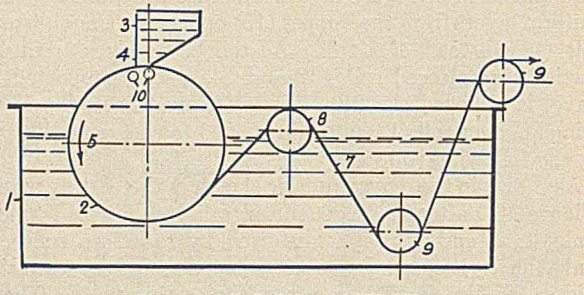

Figure 8—U. S. Patent 1,590,999

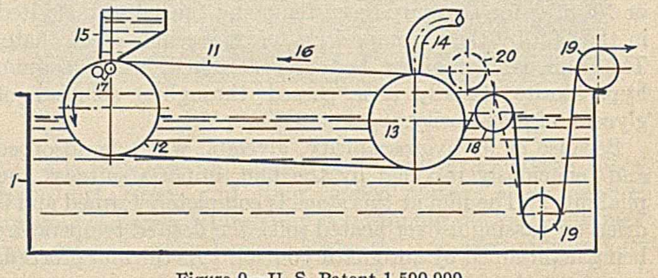

Figure 9—U. S. Patent 1,590,999

Apparatus for Casting Continuous Films

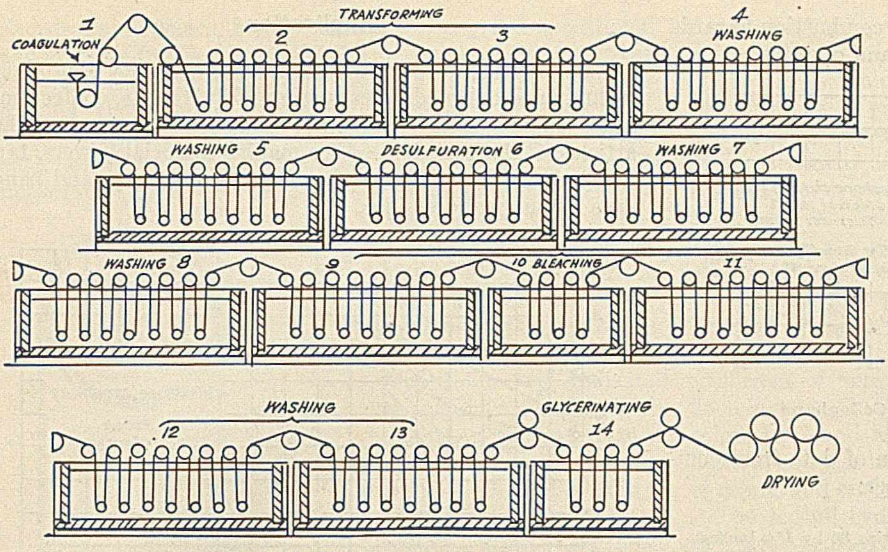

Figure 10—Diagram of Cellophane Casting Machine
(U. S. Patent 1,548,864)

disease by heliotherapy which will last at least one year and which can be replaced for a nominal sum. The curves shown in Figure 13, taken from the experiments of Pfund, evidence the fact that the transparency of Cellophane to light waves in the curative region 2900 Å. to 3100 Å. is about 70 per cent, and that, unlike some special ultra-violet transmitting glasses which lose a large fraction of their transparency on prolonged exposure to ultra-violet rays,[11] the transparency of Cellophane decreases but slightly after an exposure to sunlight for a year.

OTHER OPTICAL PROPERTIES—There appear to be two optical axes in Cellophane, such that when one observes a point of lumination through a perfectly clear film, the direction of the greatest tension during casting can be detected since the diffraction of the transmitted light is at right angles to this direction.

Cellophane exhibits the anisotropic properties of cellulose. Being thus doubly refractive, very interesting color effects are observed when Cellophane is examined with polarized light and a Nicol's prism. The polarized light passing through a Cellophane sheet is refracted and the light waves retarded according to the thickness of the film, so that a separation of the light waves results and color becomes evident. Numbers representing in millimicrons the distance retardation values have been assigned to each color and correlated with Cellophane thickness.

PERMEABILITY—Cellophane permits the rapid penetration of water vapor and of readily water-soluble gases such as ammonia and carbon dioxide. On the other hand, sparingly water-soluble gases, such as hydrogen, diffuse only very slowly through it as shown by the following table:

GAS	DIFFUSION *Liters per sq. m. per hour*
Hydrogen	0.004 to 0.02
Ammonia	Approx. 79
Carbon dioxide	Approx. 1

This characteristic permits the use of Cellophane as a semi-permeable membrane for the separation of gases from a mixture.

Cellophane, because of its relative impermeability to hydrogen, may be used as a lining for gas cells of lighter-than-air craft.

Note—**Gold beater's skin is considered satisfactory for balloon linings when it permits the passage of 0.125 liter or less of hydrogen per square meter per hour.**

In such work it is necessary to apply the Cellophane to a fabric to support it sufficiently to withstand the strains to which it is subjected. This requires special technic and special adhesives.

Cellophane may also be used as membranes for ultra-filters, permitting the separation of molecules of widely different dimensions. In dialysis work a regenerated cellulose film has been found adaptable for certain liquids where there is not excessive acidity or alkalinity.

DIELECTRIC PROPERTIES—Cellophane that is dry, free from salts, glycerol, metallic particles, and other impurities has excellent dielectric properties. When free from glycerol the film is not very pliable, however, and its successful use for condensers and other electrical equipment has not yet been developed.

In the following table are recorded data showing the dielectric values for Cellophane:

Number of layers	6
Thickness, inch	0.0039
Permeativity, untreated	4 66
Power factor, oil-treated, per cent	0.366
Corona formation, oil-treated, volts per mil	1560
Breakdown strength, volts per mil	1970

EFFECT OF AGING—Cellophane a number of years old has been found relatively unaltered in its properties except through the changes in moisture and glycerol which have occurred during that period. In other words, there is not the deterioration which is often noted in some sulfite pulp papers. Slight loss of percentage elongation is all that seems to result from the ordinary aging of Cellophane.

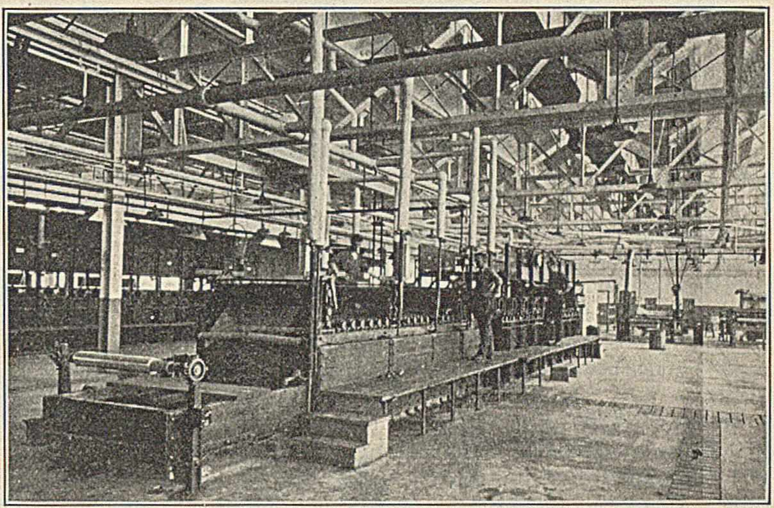

Figure 11—Cellophane Dyeing Machine

Chemical and Physiological Properties

Cellophane is a very pure regenerated cellulose and is more active chemically than natural unpurified cellulose. It undergoes the typical cellulose reactions, such as nitration, ethylation, xanthation, and swelling with caustic solution. Cellophane burns in air with a flame in a manner similar to cotton. It has been classified by the Underwriter's Laboratories

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[11] Bur. Standards, *Tech. News Bull.*, October, 1927.

(Guide No. 540–I25) as having the same combustion hazards as common newsprint in the same form and quantity.

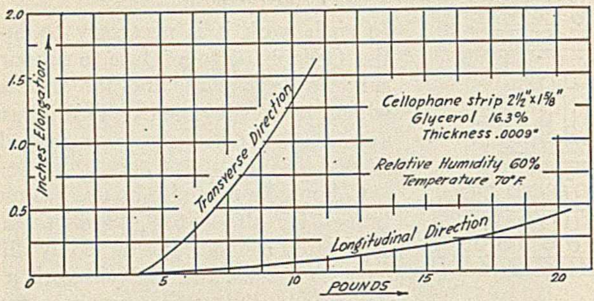

Figure 12—Physical Properties of Cellophane

The following table gives a comparison of data from combustion tests of Cellophane and newspaper:

(Average of four flammability tests made on strips 36 by $1^3/_8$ inches)

MATERIAL	TIME OF IGNITION *Second*	FLAME *Inches*	TIME OF COMBUSTION *Seconds*
Plain Transparent Cellophane	1	12	17
Moistureproof Cellophane	1	20	13
Newspaper	1	20	15

BIOLOGICAL EXPERIMENTS—Animals may be fed both Plain Transparent and Moistureproof Cellophane without harmful physiological effects. Experiments in feeding guinea pigs with Moistureproof Cellophane showed no evidence of toxic effects.

Application

Cellophane as a utility wrap is used on a variety of products including baked goods, meats, frozen fish,[12] fruits, confections, nuts, coffee, textiles, tobacco, and drugs. Among other articles, Cellophane is used for making artificial flowers, tape for stock market tickers, trimmings for millinery, and bandages for surgical dressings.

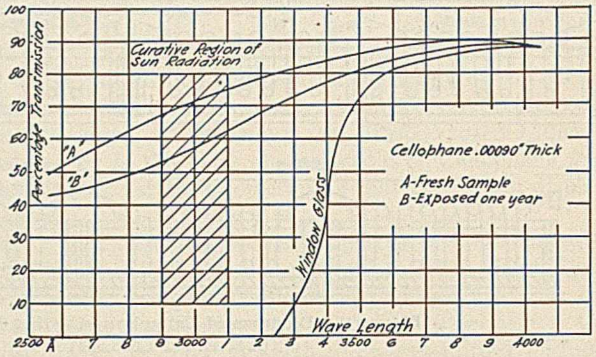

Figure 13—Comparison of Light-Transmitting Qualities of Cellophane and Window Glass

Each year the uses for Cellophane are extended into new fields so that the demand for both the Plain Transparent and Moistureproof varieties is constantly increasing.

[12] Howe, *Nation's Business*, p. 43 (February, 1929); see also Birdseye, p. 414, this issue.

Automatic Control in the Chemical Industries[1]

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PROGRESS in the chemical industries has usually been considered to be due to the establishment and development of the basic chemical and physical principles upon which a manufacturing process is founded, and to the design and construction of machinery for carrying out the operations. Chemical advancement is, therefore, dependent, not only upon the chemist, but upon the engineer as well. It is true that without the service that has been rendered the chemical industries by the manufacturer of equipment and apparatus, these industries could not have attained the positions that they occupy at the present time. On the other hand, the best designed apparatus is useless unless the chemical principles of the process carried out in it are known and applied under control, so that the best results are obtained at least cost.

It appears that the function which is played by instruments that make possible this required control has not been altogether understood or appreciated by the chemical manufacturer. He cannot avoid the use, in the plant, of instruments that measure temperature, pressure, humidity, speed, etc., but he has not used these instruments to the best advantage. The role that the measuring and recording and also the controlling instrument plays in modern industry, and in the chemical industries particularly, is becoming of greater importance from day to day. This is particularly true of the controlling instrument, for its use involves certain economies and increased efficiencies of operation which are very welcome in these days of intensive competition.

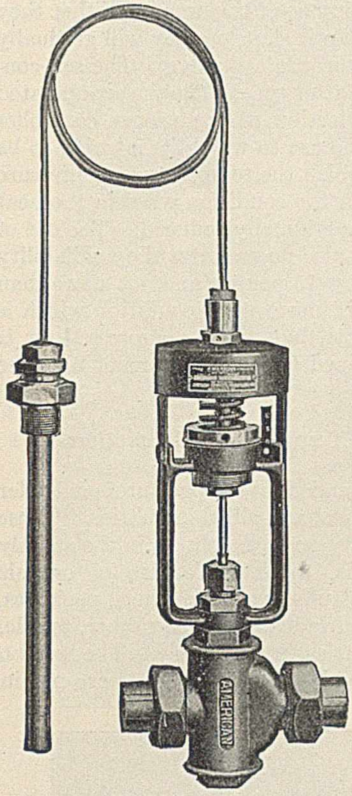
While our theme is the automatic controlling instrument, it is impossible to consider it without saying something about the other instruments as well. Indicating or simple measuring instruments merely indicate the temperature, pressure, etc., through the movement of a pointer around a circular scale as in the pressure gage and dial thermometer, by the rise of a column of liquid as in the glass thermometer, or in other ways. Indicating instruments do not interest us here, and we can leave them with just this word.

The usefulness of the dial thermometer, which measures and indicates temperature, has not been entirely appreciated by the chemical industries. The dial part of this instrument is connected by flexible tubing to the bulb, which is permanently fixed in the medium whose temperature it is desired to measure. The dial can therefore be located at any convenient point and is easily read, much more so than the column of mercury in the glass thermometer. When the temperature of masses contained in open kettles, evolving clouds of steam during the operation, has to be determined, the dial thermometer is a much more convenient and more accurate instrument than the ordinary long-stemmed glass thermometer. Reading temperatures on such a thermometer over an open kettle with steam condensing on the glass stem is not an easy or a comfortable job, or one that is conducive toward accurate readings. There are many operations in the chemical industries where the dial thermometer can be used to far greater advantage that the ordinary glass thermometer.

Controlling or regulating instruments, which automatically keep temperature, pressure, humidity, etc., at certain definite

[1] Received February 21, 1929.

and desirable points, merely control the physical conditions, and do not afford any record of the operation of the apparatus on which they are used. The recording instrument, the recording thermometer, recording pressure gage, recording tachometer, and the like, produce an indelible record of the entire operation of the apparatus. Such a record is of great importance, for it will not only tell that the temperature or pressure has been maintained at the proper points during the process, but it will also show how well the apparatus was used productively. The breaks in the recorded line will indicate time spent in charging and discharging the apparatus, and will thus show how much of the operating period is taken up with nonproductive work. Furthermore, the recorder will check the controller, and it has been found that the ideal installation is that in which both a recording instrument and a controlling instrument are used.



American Precision Temperature Controller Made by The Consolidated Ashcroft Hancock Company

Automatic Temperature and Pressure Controllers

By far the most important automatic controlling instruments used in the chemical and allied industries are the automatic temperature controller and the automatic pressure controller. The automatic temperature controller includes both instruments used for controlling low temperatures, and those used at high temperature, the automatic pyrometer controller. Sometimes, for example, in the vulcanization of rubber, it is necessary to control both time and temperature. Time-temperature controllers are used for this purpose. These instruments are designed to shut off the heating medium—steam, for example—after the temperature has been maintained for a definite period of time.

There are two general systems on which controllers of temperature and pressure are designed and operated—air-actuated and self-contained types. The self-operated type is actuated by the medium that it controls. The advantage of this instrument is that no compressed air or other auxiliary force is required for its operation. The motive power which opens and shuts the valve is supplied directly from the thermostatic system in the case of the temperature controller or by the controlled pressure in the case of the pressure controller. This motive power actuates the motor (diaphragms), which in turn operates the valve stem by expansion and contraction, thus opening or closing the valve to the heating or cooling medium. The disadvantage of the self-operated type of temperature controller is that it has a narrow range, only as high as 370° to 390° F. as a maximum. It is also not so accurate an instrument as the air-operated type, but where temperatures are low and where it is not required to maintain them within more than a 5-degree range, this instrument will work satisfactorily. The same conditions apply to the use of the self-operated pressure controller. This instrument is particularly useful in installations where steam is used as the heating medium. It is also used for reducing pressures in steam and air lines.

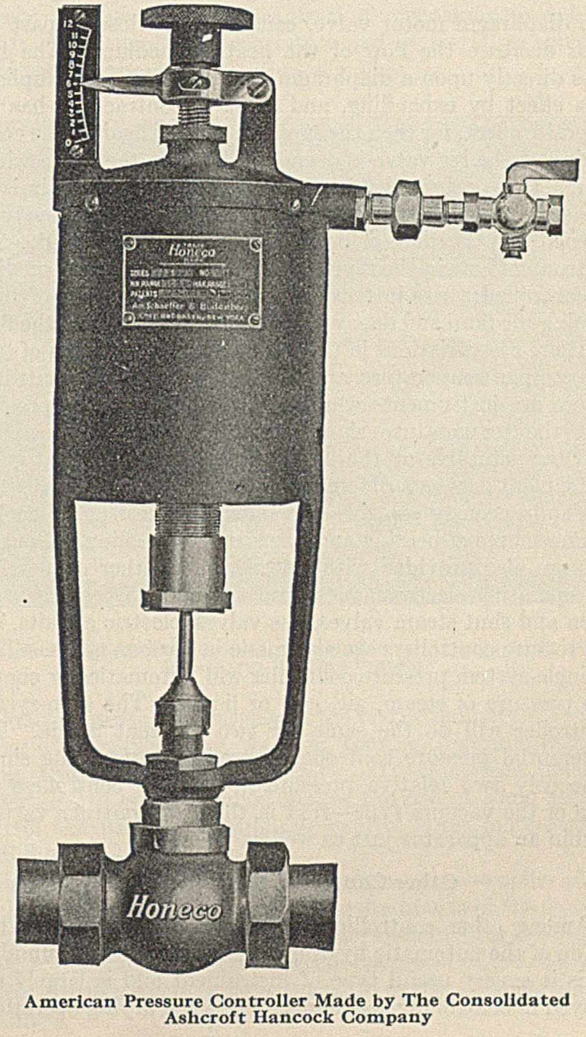
The air-operated type of controller both for temperature and pressure is an instrument which represents the finest skill and workmanship of the instrument maker. It can be made to control temperatures within a range of 1° to 2° F. Recently, new types of this instrument have appeared on the market under the name of precision controllers, and these instruments will be found satisfactory where the most stringent conditions of uniformity of temperature have to be met.

There are four general types of air-operated instruments. The first is known as the expansion stem type. Its principle is the expansion and contraction of two metals of different coefficient of expansion. This instrument does not require flexible tubing. It can, however, be used with temperatures below 100° and above 500° F. Its usefulness is, however, limited, and it is best employed in controlling the temperature of rooms and enclosures by being suspended therein.

The second type of air-operated instrument is known as the vapor tension type. It is actuated by the pressure of the vapor of a volatile liquid which is contained in the actuating system, which pressure has a definite relation to the temperature of the medium surrounding the bulb and is affected by slight temperature changes.

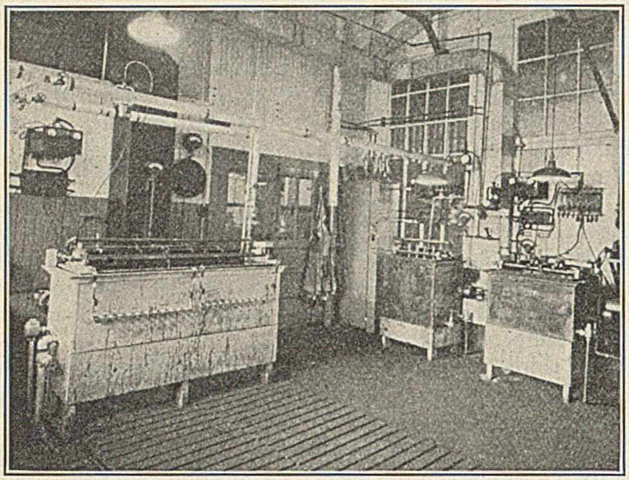
The third type is actuated by gas, this gas filling the actuating system and the pressure of the fluid, as it changes with temperature, operating the instrument.

The fourth type is the mercury-actuated instrument. This is by far the best of all the types, since mercury is a liquid which is extremely susceptible to temperature changes and



American Pressure Controller Made by The Consolidated Ashcroft Hancock Company whose expansion and contraction over a wide range of temperature remain constant. Mercury is positive and certain in its action, and is the most accurate of all the temperature controllers. The reason which makes the mercury-actuated controller so valuable an instrument is the same which makes the mercury thermometer so superior over other types of thermometers.

Air-operated controllers are not actuated directly by the change in temperature or pressure, but the pressure opens an air valve which admits compressed air to what is called the diaphragm motor valve, causing it to close in part and thus decrease the flow of the heating medium. The heat acts directly upon a diaphragm chamber which accomplishes this effect by expanding, and when it contracts it has the opposite effect, for then the pressure exerted against the coiled spring of the air valve is decreased because the space within which this pressure is exerted by the compressed air is increased and the result is that the motor diaphragm valve is opened and the flow of heating medium is increased. The instrument acts in the reverse manner when a cooling medium is controlled; rise in temperature causes the flow of more cooling medium and decrease in temperature reduces the flow.



Temperature Controller for Chromium-Plating Process

There are variations in the design and construction of both the simple temperature and the simple pressure controller. There are instruments which will control both the pressure and the temperature simultaneously. Others will control two temperatures at the same time. Still another type of instrument acts as a differential controller, which means that it simultaneously controls two sources of heating or cooling or one source of heating and one source of cooling. Controllers are also provided with electrical and other connections for operating electromagnets and the like, so that they can open and shut steam valves, gas valves, electric circuits, etc.

Pressure controllers are also made in various types. Thus a single-system pressure controller will automatically control the pressure of steam, air, gas, or liquid. The twin-system controller will do the same for two different media. The differential pressure controller is used for controlling simultaneously two relative pressures. Pressure controllers are also of the vacuum type—that is, they will control a vacuum within an apparatus just as well as pressure.

Other Controlling Instruments

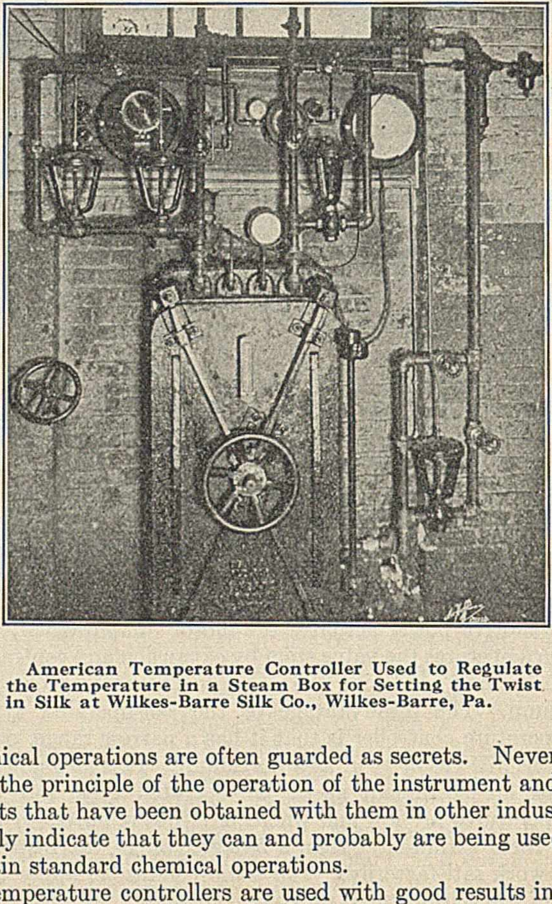
Among other controlling instruments mention should be made of the automatic hygrometer, which controls humidity. This is a very useful type of instrument and is largely employed in controlling the humidity of air in drying operations. Another very useful instrument is the automatic liquid-level controller which is designed to control the level of liquids in tanks, evaporators, etc. The automatic pyrometer controller is merely a type of temperature controller used at high temperatures.

Mechanism of Controllers

The controllers can work in one of two ways. Either they will snap open a valve or snap it shut, or they will gradually open and close it—that is, throttle the valve. The self-contained controllers are of the latter type, while the air-operated are of the former. The selection of the proper controller will depend entirely upon the use to which it is going to be put, on the accuracy with which the temperature or pressure must be regulated, and upon the condition wherein the heat must be entirely shut off or gradually reduced. The use of the air-operated instrument also necessitates the availability of compressed air at at least 15 pounds and not more than 50 pounds pressure. This is, however, a condition which is easily satisfied in most plants, but where compressed air is not available the self-contained type of instrument must be used.

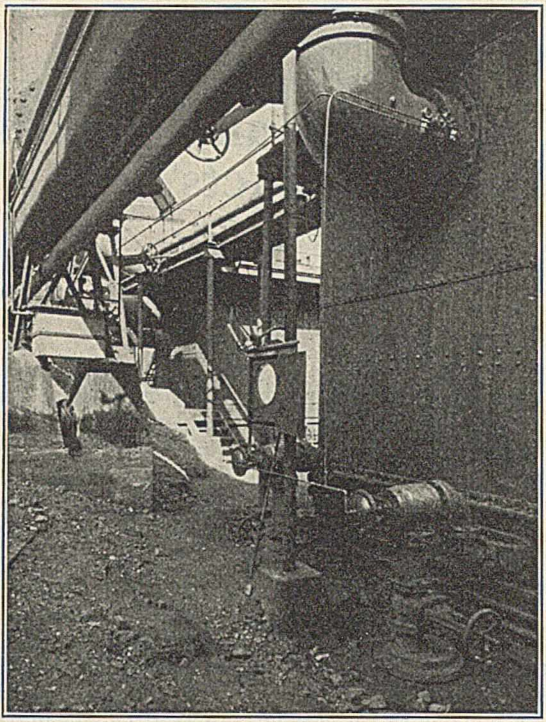
Uses of Pressure and Temperature Controllers

The pressure controller and the temperature controller find many uses in the chemical and allied industries. These uses, however, are not nearly so well defined in the strictly chemical industries—that is, the manufacture of organic and inorganic chemicals, dyestuffs, synthetic drugs, perfumes, and the like—as in the allied industries—the rubber, textile, petroleum, and food industries, for example. The reason for this is that the uses to which the instruments are put in chemical operations are often guarded as secrets. Nevertheless, the principle of the operation of the instrument and the results that have been obtained with them in other industries clearly indicate that they can and probably are being used for certain standard chemical operations.



American Temperature Controller Used to Regulate the Temperature in a Steam Box for Setting the Twist in Silk at Wilkes-Barre Silk Co., Wilkes-Barre, Pa.

Temperature controllers are used with good results in distilling operations. They may be used directly on the still to control the flow of heating medium, the bulb of the instrument being preferably inserted in the outlet leading the distilled vapors out of the still. The location of this bulb is very important and must be carefully selected if the controller is to regulate the temperature of the apparatus properly. It has been found advisable to locate the bulb in this case in the outlet pipe. In fact, this practice is followed in many other installations. There is likely to be a lag in the action of the controller due to the mass of metal which is close to the bulb. However, a simple test will enable the operator to tell just how far back he has to set the controller to compensate for this lag. There will probably be a similar lag when the bulb of the controlling thermometer is placed within a well—as for example, in nitrators, sulfonators, digesters, and the like. The space between the bulb and the walls of the well is commonly filled with a good heat-conducting liquid. Whatever lag there is in such an instance can be easily determined and allowance made for it, and should not be considered a fault of the instrument.



American Temperature Controller Regulating Flow of Water into a Gas Condenser, in a Large New York City Gas Works, to Assure Cooling of Gas to a Uniform Temperature So that Tar Extractor Can Effectively Remove Tar from Gas

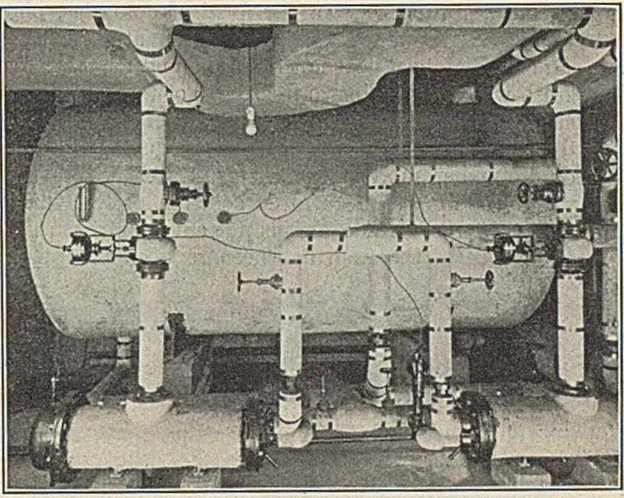
Temperature controllers have been used with good results on alcohol stills, on benzene stills in gas works, and on oil stills in the oil refinery. They can be used for all kinds of distilling operations where a definite temperature must be maintained throughout the entire process. Controllers have been used on water coolers attached to petroleum stills, rather than on the stills themselves. The controller in this instance regulates the flow of cooling water through the coils, so that the temperature is maintained just at that point where the ingredient that is being recovered will pass over in vapor form to a condenser while the other lower boiling constituents drop back in liquid form into the still.

Automatic temperature controllers—in this instance they are also called pyrometers because temperatures are high—are being used with considerable success in controlling other operations in the oil refinery, such as tower operation on cracking unit and tube still, on furnaces, pipe stills, and the like.

Temperature regulators have been used on all sorts of kettles, both of the open and closed type, for carrying out chemical reactions, such as nitration, sulfonation, reduction, etc. In all these cases a heating medium may be required to give a certain temperature beyond which bad results will be obtained. The controller will prevent too high temperatures in the apparatus. Sometimes the operation is such that the materials are first brought up to a definite temperature, when the steam must be shut off and the contents cooled down to a lower temperature or cooled to maintain them at the same temperature, the cooling being required to absorb the generated heat. A differential temperature controller may be used in this instance, first to control the flow of heat to bring the contents of the autoclave up to the desired point, and then to regulate the flow of cooling water to bring the temperature down to the desired point. This differential instrument finds many important uses in industrial operations.

Self-operated temperature controllers are particularly valuable on hot-water heaters, exhaust boxes, driers of all sorts, dry kilns, bottle washers, platen presses in the vulcanization of rubber, and the like. In fact, controllers have been found to be very efficient in regulating temperature of drying. This operation is an important one in many chemical plants, and when drying dyestuffs and other chemical products, which are easily and adversely affected by too high drying temperatures, the controller will prevent the temperature from rising too high and spoiling the product.

The pressure controller is used to regulate the flow of steam to the platen press in rubber vulcanization, to retorts, process kettles, continuous cookers, sterilizing tanks, and the like. The combination time and temperature instrument is used largely for controlling vulcanization operations in rubber plants. The combination pressure and temperature controller is used in the pasteurization of milk.



Sylphon Temperature Regulator Installed on Storage Tank of a Hot-Water Heating System

Controllers are used largely in the textile industry for regulating dyeing, bleaching, washing, souring, scouring, degumming, and many other operations. The fact that delicate materials are being handled makes the use of some sort of control essential, and automatic control is far more certain than human control.

Controllers are used for general purposes in the boiler plant of chemical works. One interesting use here is in the conversion of one kind of steam into another by removing the superheat. The controller regulates the operation of the desuperheater so that steam with a constant degree of superheat is obtained.

The paper industry uses controllers for various purposes. The instrument is used to regulate the operation of the grinder. The controller is also employed on the paper-making machine itself to regulate the flow of steam to the drier rolls so that paper with just the correct amount of moisture is obtained. This is an important matter to the paper maker, for too high moisture may mean that the paper will spoil in storage while too little will make the paper brittle.

Among the many high-temperature operations in which controlling pyrometers are employed may be mentioned galvanizing, carburizing of steel, gas-fired and oil-fired heat-treating furnaces, the blast furnace in the steel plant, core ovens in the foundry, annealing furnaces, etc.

In conclusion, it may be said that wherever heat is used and where temperature, either low or high, is important, there is a possible use of the automatic temperature controller.

Some Scientific Aspects of Packaging and Quick-Freezing Perishable Flesh Products[1]

I—More Rapid Freezing Means Better Preservation

Clarence Birdseye

General Foods Company, Gloucester, Mass.

It is the purpose of this article to contrast the characteristics of air-frozen and quick-frozen products. For present purposes air-frozen, slow-frozen, and sharp-frozen will be considered as synonyms referring to products frozen in modern "sharp freezers" with a minimum temperature of about 10° or 15° F. below zero (−23.33° or −26.67° C.). "Quick-frozen" will be used to designate products that have been frozen by direct immersion in a liquid refrigerant such as sodium chloride brine, or by indirect contact with a very cold liquid refrigerant such as calcium chloride brine.

Animal flesh is made up largely of countless elastic-walled cells filled with a semi-liquid protein gel. This gel contains a large percentage of water in which are dissolved appreciable quantities of sodium, calcium, potassium, magnesium, manganese, iron, and zinc salts in the form of chlorides, phosphates, sulfates, bromides, and iodides. Water in which these salts are dissolved does not freeze homogeneously. Instead, fresh water ice begins to freeze out of the cellular and intercellular material when the temperature of the product is lowered to about 31° F. (−0.56° C.), and, as the temperature is lowered still further, more and more fresh water ice is formed, leaving an ever more concentrated solution of the various salts. The water content of fish is not entirely frozen until the temperature of the flesh has been reduced to approximately −70° F. (−56.67° C.).

Percentage of Freezing at Various Temperatures

Complete figures are not available to show exactly what percentage of the moisture content of fish is frozen at various temperatures, but from the fragmentary evidence at hand it may fairly be inferred that a very large part has been solidified by the time the temperature has been lowered to 25° F. (−3.89° C.). From Figure 1, which shows the time required to thaw a fillet in the center of a filled 50-pound insulated shipping container, it will be noted that the temperature rise is very rapid from −10° F. (−23.33° C.) to 25° F. (−3.89° C.), the curve thereafter remaining comparatively flat until the temperature has reached about 31° F., after which it again shoots up very rapidly. Figure 2 shows that the time-temperature curve in sharp-freezing a carton of fillets is very much the same shape as that in Figure 1. Taylor[2] says that at 5° F. (−15° C.) about 15 per cent of the water remains unfrozen; while at 31° F. (35° C.) below zero, about 2.5 per cent remains liquid. Plank[3] has ascertained that at 29.3° F. (−1.5° C.) only 42 per cent of the water is frozen; while the very last of the water, which is more closely bound to the muscle colloids than the rest, is not frozen until a temperature of at least 68.8° F. (57° C.) below zero is reached. These facts have been used in the preparation of Figure 3.

Crystal Formation

During the period in which the bulk of the moisture content is being frozen, the individual ice crystals are continuously increasing in size, by accretion. After the temperature has reached 25° F. (−3.89° C.), by which time most of the water has probably been frozen, the growth of individual

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[1] Received February 8, 1929.

[2] Taylor, "Refrigeration of Fish," Appendix VIII to Report of U. S. Commissioner of Fisheries for 1926, p. 501, Washington, 1927.

[3] Plank, *Z. ges. Kälte-Ind.*, **32**, 141 (1925).

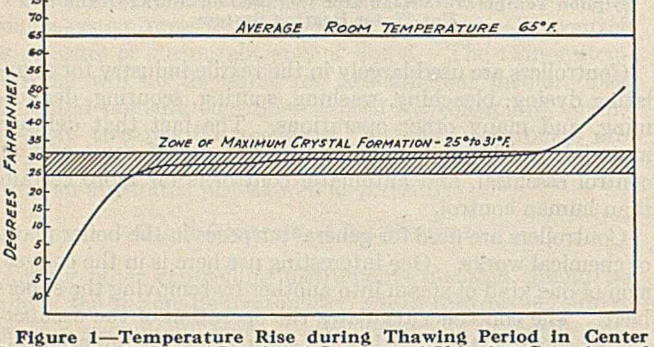

Figure 1—Temperature Rise during Thawing Period in Center Package of a 50-Pound Insulated Corrugated Shipping Container of Haddock Fillets

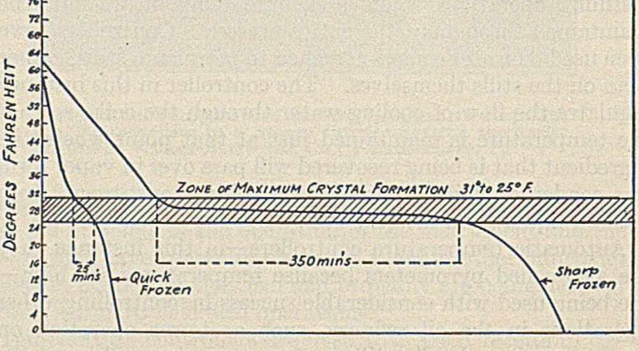

Figure 2—Time Required to Sharp-Freeze and Quick-Freeze in Center of a 2-Inch (5-Cm.) Carton of Haddock Fillets

crystals apparently largely ceases. Therefore, we may for convenience refer to the temperature zone from 31° F. (−0.56° C.) down to about 25° F. (−3.89° C.) as the "zone of maximum crystal formation." And since, when substances crystallize, the size of the crystals depends upon the time allowed for them to form, it is obvious that the more quickly flesh is passed through this zone of maximum crystal formation the smaller the crystals in the frozen product will be.

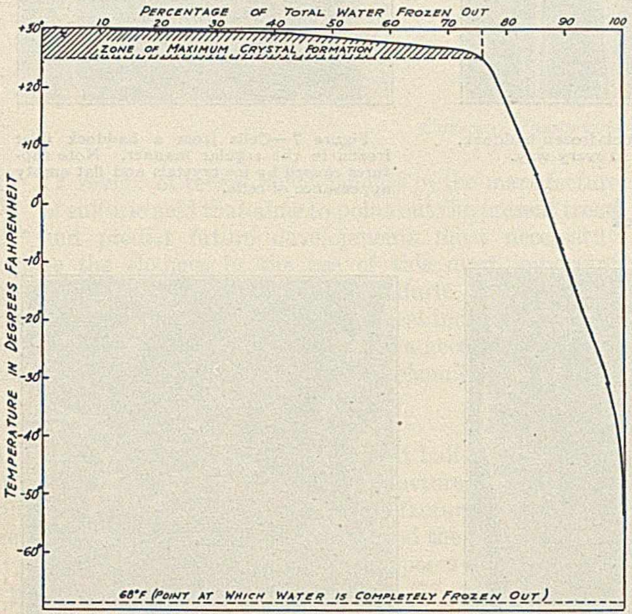

Figure 3—Percentage-Temperature Curve of Crystallization in Freezing Flesh Products

In usual sharp-freezer practice fish is frozen in from 12 to 48 hours, the heat being removed from the surface principally by convection air currents. The heat transfer is so slow that moisture at the center of the fish begins to crystallize almost as soon as that near the surface, the whole mass of the fish gradually becoming first firm and then hard. From Figure 2 it will be seen that if a 2-inch (5-cm.) package of fresh fish requires 10 hours to freeze hard in a sharp freezer, a small group (about 1 cc.) of cells in the center of the package will require approximately 6 hours to pass through the zone of maximum crystal formation. It is thus evident that in sharp-frozen fish a great deal of time is allowed for the formation of large ice crystals, which are sometimes as much as an inch (2.5 cm.) in length.

Effect on Tissues

The formation of these large sharp-pointed ice crystals within and between the cells results in a more or less serious rupture of the more delicate of the tissues and a compression of the tougher and more resistant fibers into dehydrated layers or bundles.[4] Moreover, this badly ruptured sharp-frozen flesh autolyzes more rapidly,[5] and is more susceptible to bacterial decomposition than fresh undamaged flesh.

During the comparatively slow process of sharp-freezing, a considerable amount of moisture is lost by evaporation from the surface.[6] Exact figures on the amount of this loss are not available; but it probably averages from 1.5 to 4 per cent on fish frozen in blocks, 3 to 7 per cent on singly frozen fish, and 2 to 6 per cent on bulk-frozen meats.

When flesh products are quick-frozen by direct or indirect contact with a very cold liquid refrigerant, heat is extracted from them with such extreme rapidity that, instead of being chilled almost uniformly throughout their bulk, the freezing zone advances toward the center as a sharply defined line, on one side of which the flesh may be frozen hard while on the other crystallization has not commenced. By referring again to Figure 2 it will be noted that the package of fish which required 10 hours to harden in a sharp-freezer needed only 1$^1/_2$ hours to quick-freeze. The chart also shows that, although the whole package required 6.66 times as long to sharp-freeze as it did to quick-freeze, 1 cc. of tissue at the center of the quick-frozen package passed through the zone of maximum crystal formation in 25 minutes, or fourteen times as fast as in the sharp-frozen package.

Thus quick-frozen flesh is passed through the zone of maximum crystal formation so very rapidly that the resulting ice crystals are too small to be capable of materially rupturing or compressing the tissues. The contrast between sharp- and quick-frozen flesh is clearly illustrated in Figure 4. *A* is a photograph of a piece of sharp-frozen haddock fillet cut "across the grain." This fillet was taken from near the center of a 30-pound tin of parchment-wrapped fillets of a well-known brand frozen in 36 hours in a large Boston plant. Even a casual glance at this illustration shows the serious damage done by the crystals. Much of the tissue was reduced to an amorphous mass which escaped at the cut surface when the product thawed. The remaining flesh has been compressed into tough bundles utterly incapable of re-absorbing the moisture from the melted crystals. Such a sharp-frozen piece of flesh spoils rapidly; and even when cooked immediately after being thawed, is dry, pulpy, lacking in nutrient value, and totally without the delicious flavor of the fresh product.

Figure 4-*B* shows a section of quick-frozen flesh from the center of a 10-pound package of haddock fillets. It is perfectly obvious that no large crystals were formed when this fish was frozen, and that no damage has been done to the flesh. Such a fillet, even though it may have been held in storage for several months, is still truly fresh fish.

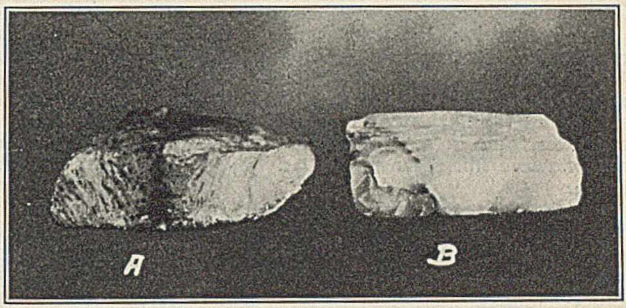

Figure 4—(*A*) Sharp-Frozen Haddock Fillet; (*B*) Quick-Frozen Haddock Fillet

Figures 5 to 10 illustrate microphotographically the damage which large ice crystals cause to individual cells of sharp-frozen haddock fillets and beef tenderloins. These photographs were taken under the supervision of R. P. Bigelow, of Massachusetts Institute of Technology. The cells of the fresh, unfrozen product are entirely normal in appearance; the quick-frozen cells show not the slightest damage from ice crystals; but the sharp-frozen cells are obviously badly ruptured. It is interesting to note that the sharp-frozen and quick-frozen haddock cells came from the fillets illustrated in Figures 4-*A* and 4-*B*, respectively.

Professor Bigelow made a further careful study of muscle tissue from fresh, sharp-frozen, and quick-frozen haddock fillets, and the following extract from his report is illuminating:

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[4] Cook, Love, Vickery, and Young, *Australian J. Exptl. Biol. Med. Sci.*, **3**, 15 (1926).

[5] Taylor, *Op. cit.*, p. 523.

[6] Peterson, *Refrigerating World*, September, 1924.

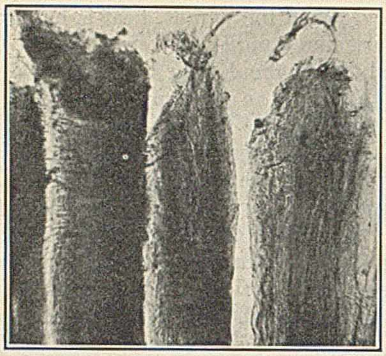


Figure 5—Cells of fresh unfrozen haddock. Note that the cells are perfect and have a full rounded appearance.

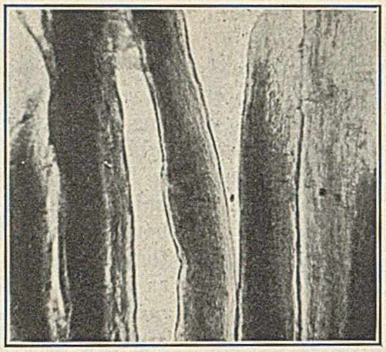


Figure 6—Cells from quick-frozen haddock. Note cells perfect in every way.

Figure 7—Cells from a haddock fillet frozen in the regular manner. Note ruptures caused by ice crystals and flat empty appearance of cells.

Haddock

Figure 8—Cells from fresh unfrozen beef.

Figure 9—Cells from beef frozen in 30 minutes in quick-freezing apparatus. Note that cells are unbroken.

Figure 10—Cells from beef frozen by ordinary commercial cold-storage methods

Beef Tenderloin

On examination, the fresh haddock appears to be well preserved. The structure of the muscle fibers is well seen, the fibrillae being quite distinct and in places the striations are visible. Between the fibers is the connective tissue. Blood vessels and capillaries can be seen, containing nucleated blood corpuscles, and in several places very beautiful pictures are seen of nerve fibers showing clearly the axis cylinder and the sheath.

The quick-frozen haddock showed apparently some disintegration of the connective tissue between the fibers, probably due to a slight maceration during the handling between the death of the fish and the commencement of freezing. But in some places the nuclei of the connective tissue can be seen and the blood vessels show distinctly the nuclei in their smooth muscle fibers. The striated muscle fibers of the muscle appear to be in good condition, showing distinctly both the fibrillae and the cross striations. In this material, as well as in the fresh haddock, the nuclei within the muscle fibers are not very distinct.

The slow-frozen haddock has a very different appearance in cross section under the microscope, as well as when seen in the hand. The muscle fibers seem to be swollen. Together with the differences in size, these muscle fibers show very different structure. In the first place, they are firmly pressed together so that only a very narrow space appears between them, and they are not evenly distributed throughout the specimens as in the case of the fresh and the quick-frozen fish. Between these masses of pressed fibers were large empty spaces, or large spaces filled with an amorphous material which may be the result of the disintegration of connective tissue. The connective tissue seems to have entirely disappeared as such from the specimen. This makes it very difficult to prepare a block for section cutting, because as soon as one attempts to cut a small piece of the flesh it falls apart. I think these slides show a very big difference between the slow-frozen haddock on the one hand and the quick-frozen and the fresh material on the other.

Shrinkage

For obvious reasons, loss of weight by evaporation during quick-freezing by any of the better known methods is very much less than in sharp-freezing. When the products are properly protected by highly vapor-proof packages before being frozen, the shrinkage is negligible. At one large quick-freezing plant the average shrinkage in freezing haddock fillets wrapped in Moistureproof Cellophane and packed in 10-pound cartons is less than 0.25 per cent.

Table I shows that there was practically no shrinkage in various packaged dressed meat products experimentally quick-frozen at the above plant.

Table I—Loss of Weight during Quick-Freezing of Certain Packaged Meats

PRODUCT	BEFORE FREEZING		AFTER FREEZING	
	Lbs.	*Oz.*	*Lbs.*	*Oz.*
Sirloin steaks	11	$4\frac{1}{8}$	11	$4\frac{1}{8}$
Pork chops	5	$12\frac{3}{4}$	5	$12\frac{1}{2}$
Beef tenderloin	5	$10\frac{3}{4}$	5	$10\frac{3}{4}$
Lamb chops	5	$12\frac{1}{2}$	5	$12\frac{1}{2}$
Lamb kidneys	6	$6\frac{1}{2}$	6	$6\frac{1}{2}$
Calves liver	6	$3\frac{3}{4}$	6	$3\frac{3}{4}$

Other Advantages of Quick-Freezing

When certain forms of meats and poultry are sharp-frozen, the extensive drying of the surface, sometimes apparently associated with a partial oxidation of the fats in and immediately under the skin, causes an effect known as "freezer-burn," which considerably lowers the value of the products. Freezer-burn was entirely absent in the packaged meats considered in Table I, and did not occur even with such bulk products as green pork bellies frozen in direct contact with the metal belts of the quick-freezing apparatus. Perhaps equally important, from the marketing point of view, was the fact that the color and odor of the packaged meats was not changed at all by the quick-freezing. "Drip"—leakage of moisture from the product during the thawing process—was very slight indeed.

Recent Developments in the Manufacture of Sulfuric Acid[1]

S. F. Spangler

Chemical Construction Co., Charlotte, N. C.

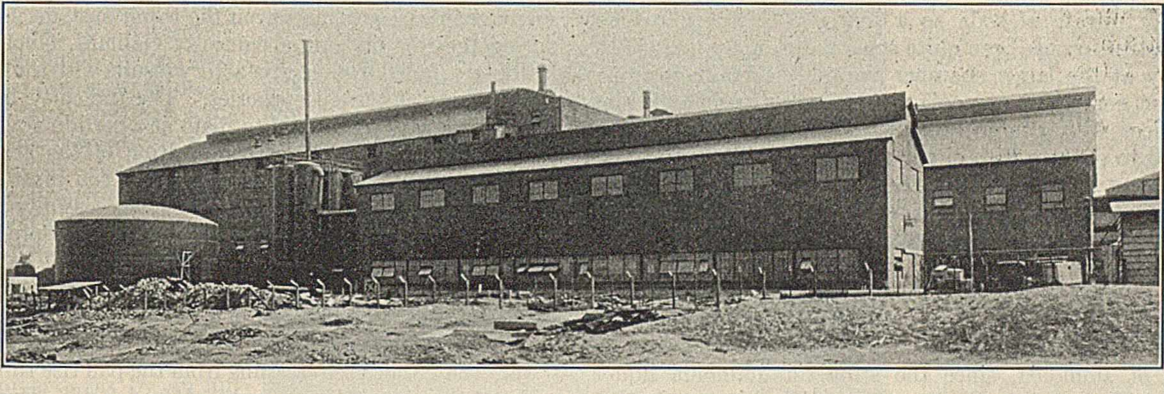
Any review of recent developments in the manufacture of sulfuric acid that aims to point out the present trend and predict future developments must necessarily recognize the changes in the use of this most important chemical in the last few decades. Sulfuric acid has been recognized since the beginning of chemical industry as being one of the most important chemicals and a necessary material in the manufacture of very many other chemicals.

Chamber Plants

At the beginning of this century about half of the sulfuric acid produced was used in the manufacture of phosphate fertilizers and the remainder in the manufacture of explosives, oil-refining, the pickling of steel plate, and the preparation of heavy chemicals. For most of these purposes the lead chamber plant producing an acid of 60° Bé. (77 per cent H_2SO_4) strength was the most suitable and most common type of plant, since only 52° Bé. strength of acid is required in the fertilizer trade. The stronger "oil of vitriol" or 66° Bé. (93 per cent H_2SO_4) acid was made, when required, by concentration of 60° Bé. acid by direct heat in retorts or cascade concentrators. If an especially pure, strong acid was desired, such concentration was effected in glass or platinum vessels. The comparatively small requirements for fuming sulfuric acid—i. e., acid of over 100 per cent H_2SO_4 strength—were taken care of by a few scattered contact plants employing platinum mass as the catalytic agent, with none too satisfactory an efficiency. The usual source of the sulfur dioxide gas used in both chamber and contact plants was iron and copper sulfides (pyrites), which commonly were roasted in brick ovens. To a small extent brimstone was used as a source of the sulfur dioxide gas by direct combustion in similar ovens.

The rapid development of the explosives industry during the war period caused an enormous increase in the demand for sulfuric acid. The "mixed acid" used in the manufacture of explosive nitro compounds required sulfuric acid both as one of its direct constituents and indirectly in the manufacture of nitric acid, the other constituent. For the manufacture of nitric, a sulfuric acid of 66° Bé. strength was required, while fuming acid was the most suitable form of the sulfuric acid used as a direct constituent of the mixed acid. The result of the war demand was to compel operation of all existing chamber plants in excess of their normal capacity, the rapid building of various types of concentrating plants to produce 66° Bé. acid from chamber plant acid, and a large increase in the number of contact acid plants. This period saw the successful application of acid-proof masonry in this country to the construction of the Glover and Gay-Lussac towers of chamber plants and of tower types of concentrating plants on a large scale and the shift from pyrites to brimstone as the principal source of sulfur dioxide gas. This latter shift was accompanied by the replacement of brick furnaces by more efficient types, such as the rotary Glens Falls burner and the Vesuvius burner. Such plants as continued to use pyrites as a source of sulfur dioxide generally replaced their brick ovens with mechanical furnaces of the Herreshoff or Wedge type. The contact acid plants continued to use platinum as the catalytic agent and the sudden scarcity of platinum caused by the war demands will not soon be forgotten by the chemical industry.

With the close of the war the demand for 66° Bé. and fuming sulfuric acids declined rapidly, though the subsequent growth of the dye industry eventually brought a resumption of the demand for mixed acid. The fertilizer industry continued to demand chamber plant acid, but the depression in the fertilizer trade forced many of the weaker plants out of business and prevented expenditure of funds for all but the more urgent repairs. A new factor came into the industry in the increase in the demand for sulfuric acid from the rapidly expanding oil industry. This called not only for additional



Contact Acid Plant Showing Very Compact Arrangement Compared with Chamber Plant of Equal Capacity in Background

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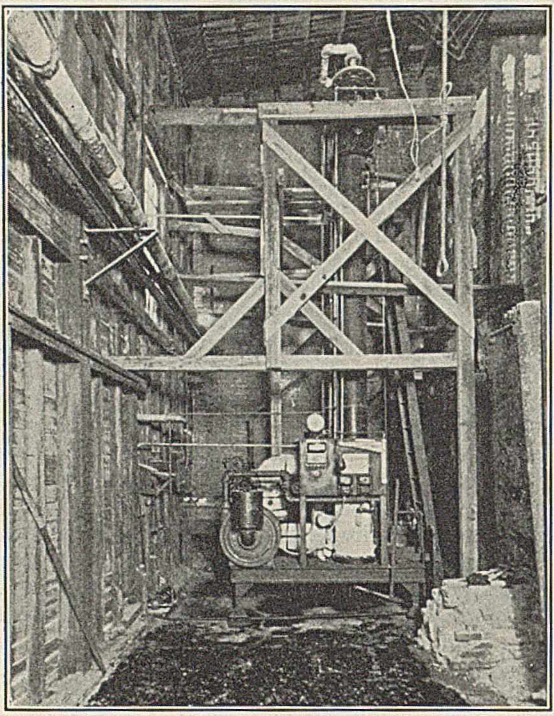
[1] Received March 11, 1929.

quantities of sulfuric acid to be manufactured, but for better recovery and concentration of the weak sulfuric acid contained in the acid sludges produced by the treatment of the oils with strong sulfuric acid. In addition, a change in the character of the oils treated called in many cases for a stronger acid and brought contact plants into the acid departments of oil refineries. All this was accompanied by a growing demand for more efficient and economical plant operation, with the result that the old processes were subjected to searching examination and radical modification by the leaders of the acid industry.



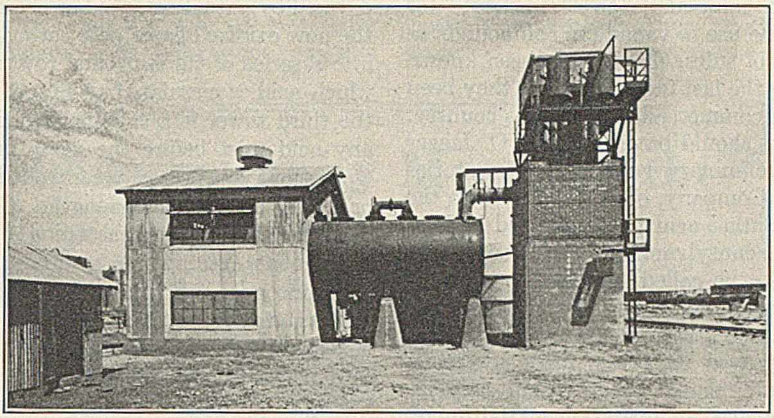
Ammonia Oxidation Unit Installed in Chamber Plant of a Florida Fertilizer Works

During the last few years the most noticeable change at sulfuric acid chamber plants has been the substitution of ammonia for nitrate of soda as a source of nitrogen oxides. This substitution has been quite general during the past year, especially at the larger chamber plants. Several companies now offer complete ammonia oxidation units installed at fixed prices with guaranteed results. These units can be furnished to operate with either anhydrous ammonia or ammonia liquor. As several articles have appeared recently describing these oxidation units in detail, such description will be omitted in this review. It might be stated that the majority of the oxidation units now in successful operation in this country employ the cylindrical or Parsons type of platinum gauze as the catalytic agent. The use of pure anhydrous ammonia offers the advantage of reduced freight expense on receipts of ammonia, since the strongest ammonia liquor transportable contains only 30 per cent NH_3, but has the disadvantage of requiring expensive high-pressure storage tanks. In addition, the units employing ammonia liquor are simpler to control—a decided advantage with the average grade of chamber plant operator—and their platinum gauzes are less quickly poisoned by impurities in the air, since the air is subjected to an alkaline washing by the ammonia liquor in the stripping column. A recent development in connection with ammonia oxidation units has been the perfection of a simple mixing nozzle through which anhydrous ammonia may be discharged into water inside an ordinary closed cylindrical tank and converted into ammonia liquor with only a negligible loss. The use of this nozzle permits the installation of the more efficient ammonia-liquor type of oxidation unit and the cheaper ammonia-liquor storage tanks to be combined with the purchase of the ammonia as anhydrous ammonia at advantageous freight rates, and probably foreshadows the settlement of the question of the most suitable type of oxidation unit for chamber plants.

The other change of interest at chamber plants has been a gradual reduction of chamber space per unit of acid production capacity. In the majority of cases this has been done by the introduction of closely packed intermediate towers between the chambers, but two manufacturing companies have adopted the Mills-Packard system of chambers, a system of externally water-cooled conical lead chambers giving an intensive reaction and requiring a limited floor space. In the case of one of these companies, Mills-Packard chambers have been installed at three different plants and a considerable increase of production per unit of chamber space has been secured. Unfortunately, this is also attended by increased operating difficulties, which necessitate closer supervision. The other intensive European systems, such as the Gaillard turbo-disperser and the Schmiedel roller box, have not found favor in this country, principally because they require too close technical supervision. As previously pointed out, the chief field of the chamber plant in this country is as a source of supply of weak sulfuric acid for the fertilizer industry, and the fertilizer industry as a whole is still in the stage of rule-of-thumb methods as far as acid-making is concerned. There are, of course, some notable exceptions, but they are among the larger plants. For the smaller plants dependent on cheap labor, the use of any extremely intensive chamber system is inadvisable, as possible operating losses can quickly overbalance savings in original investment.

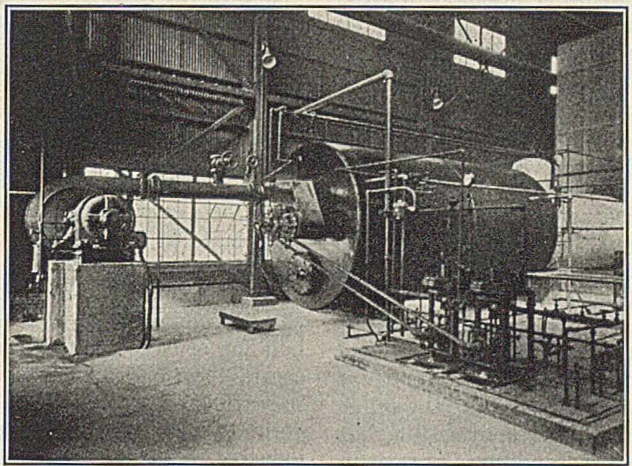
Improvements in Concentration

Before considering the developments in contact acid plants, it seems desirable to devote a few lines to the recent improvements in the concentration of moderate strength sulfuric acid to strong sulfuric acid. As previously stated, the growing requirements of the oil industry have been responsible for the greatest improvements in this line. The older processes of concentration, such as direct heat under dishes and retorts singly or in cascades, and even the tower systems so popular during the war under the names of Gaillard, Gilchrist, and Kalbperry, failed to give satisfactory results with the separated sludge acids of the oil refineries. The difficulty lies in the tendency of the sludge acid to foam at a certain stage of concentration, owing to the decomposition of the acid by the carbonaceous materials present in even the most carefully separated sludge acid. This was first successfully overcome in 1920 by the use of the two-stage submerged-pipe process. In this process combustion gases from a forced-draft oil furnace are forced at a temperature of about 1100° F. under the surface of the acid contained in a covered acid-proof masonry pan communicating with an acid-proof masonry preheating tower, where the gases escaping from the pan rise through and preheat the descending supply of feed acid. Evaporation takes place in the pan at less than the ordinary boiling point of the acid, since the effect of blowing the hot gas through the acid is similar to operating under a partial vacuum. The process is divided into two stages with identical pans and towers, and both stages are usually supplied from one oil furnace. In the first stage the acid is concentrated from about 30° or 35° Bé. to between 50° and 55° Bé. strength, and much of the carbonaceous matter is removed by either volatilization or oxidation. This 50–55° Bé. acid, after passage through an intermediate storage tank, where some of the remaining carbonaceous matter is removed mechanically, becomes the feed acid for the second stage, where it is concentrated to 66° Bé. strength. The waste gases leaving the towers of both stages are combined and passed through a Cottrell electrical precipitator to condense any sulfuric acid mist as weak acid which is returned to the process.



Drum-Type Concentrator

During 1928, the company controlling the basic patents of the two-stage submerged-pipe system has introduced a modification known as the drum type of sulfuric acid concentrator, which has several advantages over the earlier tower type. In the drum-type concentrator the arrangement may be described as being a "series" flow as compared with a "parallel" flow in the older type. In the new type the exit gases from the high, or second, stage are passed into the low, or first stage, whereas, in the older type both stages received hot gases separately from the furnace. The expensive high preheating towers are eliminated entirely. The apparatus consists essentially of a long, horizontal steel drum divided into three compartments. The front compartment is lined with insulating and fire brick and equipped with an oil or gas burner operated under forced draft furnished by a centrifugal air blower. The other two compartments are lined with heavy sheet lead and acid-proof brick and cement. The hot gases leave the combustion chamber at a temperature of around 1100° F. and enter the middle or high-stage compartment, where they are released beneath the surface of the acid bath. The gases leave this chamber at about 450° F. when acid of 66° Bé. is being made in the high stage. These gases, containing a small quantity of sulfuric acid mist, then enter the rear or low-stage compartment where they are again released beneath the surface of the acid and emerge at a temperature of 200° to 300° F., depending on the strength of the feed acid supplied to this compartment. The gases from the rear compartment are cleaned before being released to the atmosphere by passage through an electrical precipitator or some equivalent absorption or scrubbing tower. The flow of acid is countercurrent to the flow of gases. The weak acid is fed continually into the rear or low-stage compartment by an air lift or pump. When fresh or moderately clean sulfuric acid is being concentrated, the acid from the rear compartment flows by gravity through luted passage into the middle compartment. When a sludge acid is being handled, the acid from the rear compartment flows into an intermediate storage tank through a skimmer, where the non-volatile carbonaceous matter can be skimmed off, after which the resulting intermediate strength acid is pumped by an air lift into the middle compartment. From the middle compartment the strong finished acid is drawn off through a cooler into storage tanks. The operation is continuous, since the violent agitation of the acid inside the compartments caused by the passage of the hot gases prevents the settling out of any residue inside the drums. Obviously, the use of the waste gases from the high stage as a source of heat for the low stage gives greater heat economy than was possible in the earlier tower system, where the low-stage unit received direct furnace gases and the gases from the high-stage unit escaped. Control of the entire operation is from one centralized control board provided with necessary indicating or recording pyrometers, gages, etc. While the drum type of concentrator has been available only since the beginning of 1928, nearly a dozen are already in operation. The majority of these are in connection with oil refineries, but several are in use handling the residual sulfuric acid produced in the concentration of nitric acid as an adjunct of synthetic nitric acid plants.



Pressure-Type Furnace for Molten Sulfur

An interesting development in connection with Cottrell electrical precipitators for sulfuric acid mist has resulted directly from the use of the drum-type concentrators with residual sulfuric acid from nitric acid concentration plants. This residual sulfuric acid is liable to contain a small trace of nitric acid, which is dangerous to the lead tubes and chambers of the ordinary type of precipitator. Recently four electric precipitators have been completed where the chambers are of acid-proof masonry and the tubes of high-silicon iron. The electrode wires remain lead as formerly, but occasional replacement of these wires is a simple matter compared with replacement of lead tubes and chamber walls. These precipitators have proved so satisfactory that high-silicon iron tubes are being chosen for all precipitators built in connection with drum-type concentrators, whether or not there is danger of the presence of nitric acid, because of the longer life of the iron tubes.

The only other process now being installed to any extent in new plants for the concentration of separated sludge acid is the vacuum process. Two different vacuum concentrators are available from reputable construction companies. It is the writer's opinion that neither is especially adapted to producing satisfactorily an acid of 66° Bé. strength because of mechanical difficulties. Where a product of only 60° to 63° Bé. strength is required, the vacuum process has the decided advantage of not requiring any precipitator or equivalent fume eliminator, but the tendency in the treatment of oils is toward the use of acid of 66° Bé. and stronger.

Contact Process

By far the most noteworthy recent change in the contact process for the manufacture of fuming sulfuric acid has been the adoption of vanadium compounds as a substitute for platinum as a catalyst. The use of vanadium compounds as catalysts for the oxidation of sulfur dioxide has been known since 1895, but only during the last few years have they been employed successfully on a commercial scale in this country. Credit for this development should be given to A. O. Jaeger and his associates, whose preliminary work in the laboratories of the Monsanto Chemical Company, of St. Louis, led to the erection of five different contact acid plants located in East St. Louis, Ill., Oklahoma, Pennsylvania, and Wisconsin—all employing what has come to be called the Monsanto vanadium mass. Doctor Jaeger subsequently became associated with the Selden Company, of Pittsburgh, Pa., where further research developed an improved vanadium mass now marketed as the Selden vanadium mass. The first plant employing the Selden mass was placed in operation at Baltimore, January, 1928, and since then construction of eight plants having a combined capacity in excess of 800 tons of 100 per cent acid per day has been begun, while plans are being prepared for several other large installations. As compared with platinum mass, the vanadium mass possesses the advantages of cheapness, immunity to poisoning by arsenic and substances detrimental to platinum mass and, when used in properly designed converters, the high average conversion efficiency of 97 to 99 per cent. While it has been claimed that platinum mass freshly activated and under extremely close technical control may give equally high conversion efficiency, there appears to be no question that the average conversion efficiency in actual operation in commercial plants with platinum mass is rarely over 92 per cent due to the ease with which platinum mass is poisoned by the common impurities present in sulfur dioxide gas.

Exclusive rights to the erection in this country of plants using the Selden mass are held by one construction company whose engineers are responsible for some interesting departures from the conventional arrangement of contact plants using platinum mass. Probably the most important new feature is the use of a patented type of sulfur furnace, burning molten sulfur sprayed in through a burner which in many respects resembles the common mechanical oil burner. Air, thoroughly dried by passage through a scrubbing tower fed with strong sulfuric acid and then freed of any acid mist by passage through a packed filter tower, is forced into the furnace by a centrifugal blower. This blower furnishes all the air required for combustion and all the pressure required for driving the gases through the rest of the system. The strength of the sulfur dioxide gas produced in the furnace can be regulated perfectly by control of the air supplied by the blower and the quantity of sulfur burned can be regulated by the variable speed of the sulfur pump. The hot sulfur dioxide gases from the furnace pass through a boiler, where they serve to generate the steam used in melting the sulfur. This boiler at the same time reduces the temperature of the burner gases to such an extent that only a comparatively small additional sulfur dioxide cooler is required to reduce the gas to a temperature suitable for entering the converters. Melting the sulfur before introducing it into the furnace removes, by settling out in the melting tanks, most of the dirt, sand, etc., present in the sulfur. To remove any dust mechanically carried over, the combustion gases are passed through a packed filter tower, which, however, is of far smaller and cheaper construction than is necessary in the conventional arrangement. The converters used in this process are of a newly developed design especially adapted for use with the vanadium contact mass and involve heat exchanger tubes inside the body of the converter which permit close regulation of converter temperatures. These converters have been successfully operated in sizes up to 40 tons equivalent 100 per cent H_2SO_4 per day. Like the other new features of this process, they are fully covered by patents granted or pending. From the converters the now oxidized gases pass through a "SO_3 cooler" and then into a series of three packed towers through the first two of which acid is circulated to absorb the sulfur trioxide, while the third tower is a coke-packed filter tower which removes any acid mist before the gases finally escape into the air. Operations can be easily controlled to give acids of 109, 104, or 98 per cent H_2SO_4 strength. Control is from one central room containing the recording pyrometers, gas analytical instruments, etc., which results in a saving of labor so that only one operator with a helper for wheeling sulfur, oiling motors, etc., is required per shift. The entire plant occupies considerably less ground space than the older types of contact acid plants or than chamber plants of equivalent capacity. Owing to the lower initial investment, it is possible to produce 66° Bé. acid, and even in most cases 60° Bé. acid, by dilution of the fuming acid produced in this new type of contact plant at less cost than by the older chamber process.

The use of vanadium mass instead of platinum mass has been universal in all new contact acid plants erected in this country during the last year, with the possible exception of enlargements of former plants made by certain of the larger chemical companies with long experience and heavy investments in platinum-mass type plants. As a result of their past experience, these companies are in the best position of any to secure maximum efficiences and low costs with platinum-mass type plants, and their present heavy plant investment operates to prevent any sudden change to the newer type. For the present this question may best be passed by observing that the new vanadium-mass type plants are being erected in market territory formerly considered the exclusive preserve of these older companies.

Future Trends

While the advances in sulfuric acid technology during the past few years which this article has attempted to outline have been of considerable extent, it must not be assumed that perfection has been attained. There is still room for great improvement, not only in major details of the processes, but in the accessory equipment. It is always dangerous to prophesy future trends, but it may be interesting to attempt it. The ability of the new types of contact acid plant to produce cheap 66° Bé. acid definitely foreshadows the passing of the sulfuric acid concentrating plant except for the handling of sludge and spent acids. It probably eliminates the chamber plant as a source of marketable acid—why pay freight on water?—and reduces the probability of building new chamber plants at fertilizer plants except where small requirements, ready access to sources of sulfur and distance from existing contact acid plants combine to raise the cost of purchased fuming acid. The logical trend appears to be the building of large vanadium-mass-type contact acid plants at central locations, and the shipping of fuming acid from these to scattered fertilizer plants, where it would be diluted to the desired degree, thus reducing the acid problem of the fertilizer industry to the matter of a few storage tanks. For the oil industry there is a growing tendency to use strong acid (66° Bé. and 98 per cent H_2SO_4) in treating which points logically to contact acid plants combined with concentrators capable of bringing the weak separated sludge acid up to full 66° Bé. strength, which can then be used either as the absorbing acid in the contact plant or fortified with fuming acid to give a 98 per cent acid or used as 66° Bé. acid.

At least one major problem remains unsolved and its correct solution may upset all current predictions regarding sulfuric acid. The waste liquor from the pickling tanks of the steel industry contains an enormous quantity of ferrous sulfate. If this can be economically converted back into sulfuric acid, conditions in the industry will be materially changed. Considerable research has been done on this problem in recent years, and it is understood that several possible processes are now ready for trial on a commercial scale.

Mechanical Dispersion by Means of the Colloid Mill[1]

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The application of mechanical devices in the process industries is constantly making possible today what was impossible yesterday. So rapid has been the progress that the best methods of ten years ago are now antiquated, as probably within five years more the best methods of 1929 will have been supplanted with still better ones. In our hurry to keep up with the stream of contemporary developments we are, however, often subjected to the hallucinations of overenthusiastic salesmen. One of the really important devices which has suffered greatly from false claims and ill-conceived applications is the so-called "colloid mill." This article will attempt to explain the true nature and function of the colloid mill, indicating its limitations as well as its points of particular significance to the chemical engineer.

In the first place it would be well to state the basic viewpoint that the mechanical equipment which is referred to as a "colloid mill" represents not more than 20 per cent of any problem involving its use, the remaining 80 per cent representing the fundamental knowledge of physical chemistry which is necessary for the successful application of this equipment to mechanical dispersion. At present there is a lack of trained technicians in this new field, and the colloid mill has accordingly suffered. Where it has been used improperly it has failed, and the result has been unjust and bitter criticism of the mechanical apparatus, instead of just criticism of the ignorance of fundamental scientific principles commonly exhibited by equipment salesmen.

The colloid mill began its existence under an unfavorable star, for its very name has been the basis for much misunderstanding. It was at first thought that mechanical dispersion of material to colloidal dimensions was feasible; hence the name "colloid mill" was applied to the apparatus intended to accomplish this dispersion. The generally accepted upper limit of particle size for the colloidal state is, however, a diameter of 200 mμ, whereas the colloid mill rarely disperses to a particle diameter of less than 1μ. Particles of this size are, to be sure, in a sort of twilight zone in which they exhibit many of the properties of the colloidal state. It would be much more accurate, however, to refer to the mechanical equipment which produces them as a dispersion mill rather than a colloid mill. The name "dispersion mill" further serves truth by indicating that such equipment is, in reality, a dispersing mechanism, and not a fine grinding mill as it is popularly misconceived.

The History of the Colloid Mill

Although Plauson[2] has generally received the credit for building the first colloid mill, the literature shows that the idea was anticipated by von Weimarn as early as 1906,[3] and the latter has stated that he built a colloid mill for laboratory use in 1912. It was originally von Weimarn's belief that colloidal dispersions could be obtained by mechanical grinding or shearing actions if some stabilizer were present to exert a protective action on the particles produced.

About 1916, also before any commercial development of the Plauson mill, inventors were busy with the question of dispersing solid hydrocarbons in oils for the purpose of making liquid fuels. There are frequent references during this period to "high-speed" mills, some optimistic but erratic individuals proposing peripheral speeds of 200,000 feet per minute. At this time it was recognized that high speeds were necessary to obtain proper hydraulic shearing action, the action which has since become the most important factor in the development of the colloid mill.

The Plauson machine, which in spite of von Weimarn's prior claim on the idea of a colloid mill nevertheless deserves great credit as the first actual attempt at a machine for industrial use, has never been used to any extent in this country. Subsequent to its appearance, however, rapid development of other types of mills began, both in Europe and in the United States. In the following section a classification of colloid mills will be made on the basis of the mechanical details of the working surfaces.

Classification of Colloid Mills

A sharp distinction should be drawn between the pressure type of homogenizer and the colloid or dispersion mill. The well-known pressure type of homogenizer, utilizing pressures of from 2000 to 3000 pounds per square inch, has been used for many years in the dairy industry, and has also been applied in pharmacy to the making of simple emulsions. It is not suitable, however, for the dispersion of solids or for the emulsification of heavy liquids. This type of equipment has been confused with the colloid mill because some of the modern machines of the latter type have been described as "homogenizers," an appellation which is undoubtedly true in itself but by its connotations leads to unfortunate confusion between two entirely different types of apparatus. The pressure homogenizer will not be discussed in this article.

The colloid or dispersion mill, as referred to herein, is a machine that depends essentially for its dispersive action upon hydraulic shearing forces exerted on particles suspended in a fluid medium. Although some pressure is created within the machine, it is much lower than that necessary for the operation of the pressure homogenizer and is secondary instead of being the main factor in producing dispersion.

Colloid mills may be classified in three main groups with regard to the mechanism utilized for producing dispersion. These groups may be called the beater type, the smooth-surface type, and the rough-surface type.

Beater-Type Mills—The beater type includes the original Plauson machine and some of the modified machines derived from it. In these mills the particles to be dispersed are subjected, not only to hydraulic shearing stresses, but also to impact stresses produced by revolving blades entering and leaving the spaces between fixed blades. The power

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[1] Received August 4, 1928.

[2] Plauson, U. S. Patent 1,500,845 (application April 22, 1921; granted July 8, 1924).

[3] Von Weimarn, *J. Russ. Chem. Soc.*, **38**, 466, 470 (1906); **39**, 619 (1907).

requirements of the original Plauson were excessively high and it was operated only as a batch machine—factors which opposed its adoption in industry, although the results obtained with it were excellent. The various modifications of this type of machine have attempted to overcome its original defects, the Oderberg machine recently described[4] claiming a power requirement decrease to one-seventh of that of the original Plauson mill for equal capacities.

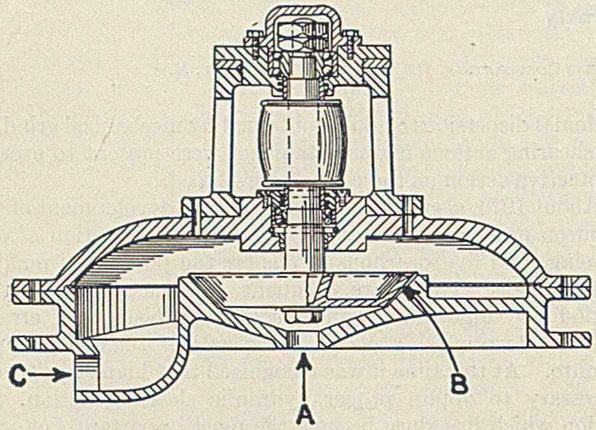

Figure 1—Smooth-Surface Type of Colloid Mill with Truncated-Cone Working Surfaces

A—Material inlet; *B*—Working surfaces; *C*—Material outlet

Smooth-Surface Type—This type of machine depends only upon hydraulic shearing forces for its effect. Machines of this type consist of a smooth moving surface which passes a smooth fixed surface at a high velocity (2 miles per minute or higher) and with a small clearance (0.002 inch minimum). The adsorption of films of fluid upon each of the working surfaces causes tremendous shearing stresses in the rest of the thin layer of liquid between them. These stresses are responsible for the dispersion of the particles of material suspended in this layer. Operation is continuous with these mills, but the rate of flow between the working surfaces differs in different machines. One variation maintains a steady flow of material past the working surfaces by means of centrifugal force, while a second modification has its working surfaces so shaped as to delay the movement of material past them. While the time that the material is actually on the working surfaces is only a fraction of a second in any case, it is several times longer in the second case than in the first.

Centrifugal smooth-surface mills have as their working surfaces either a truncated cone rotating within a fixed cone or flat disks rotating in opposite directions. This class of mill is generally mounted on a vertical shaft, as in the truncated-cone type shown in Figure 1. In the particular mill illustrated the material is fed from the bottom, passes between the working surfaces, and is thrown off at the top owing to the increase in centrifugal force as the diameter of the rotating surface increases. The flat-disk type of machine, sometimes known as the English Plauson, is shown in Figure 2. This machine is fed through its axis, the material passing between the oppositely rotating disks, and being thrown off from their periphery into a chamber, from which it is removed by gravity.

Delayed-action smooth-surface mills have cylindrical or nearly cylindrical working surfaces and are usually mounted on a horizontal shaft. Inasmuch as the peripheral speed varies but slightly over the working surfaces, the material being treated tends to remain between these surfaces a longer time than in the centrifugal-type machines. Figure 3 shows a cross-sectional view of a delayed-action colloid mill with smooth, nearly cylindrical surfaces. Material is fed to the working surfaces through channels in the rotor.

Rough-Surface Type—The third class of colloid mills is distinguished by the use of roughened working surfaces, which add to the hydraulic shearing action a second dispersing action of intense turbulence and beating produced by eddy currents in the liquid between the irregular surfaces. Aside from the use of roughened surfaces, this class of mill is quite similar to the centrifugal smooth-surface type, as the working surfaces are arranged either as truncated cones or opposed disks. Figure 4 illustrates in cross section a mill in which conical working surfaces covered with grooves are used, while Figure 5 shows the parts of a machine in which the working surfaces are disks.

Turbine-Type Mill—A machine which embodies features of both the smooth-surface and rough-surface types is shown in Figure 6. This mill is called a turbine-type machine. It is somewhat handicapped by the fact that the clearance cannot be adjusted to take up wear, but has the advantage of an intensive and prolonged dispersing action.

Industrial Utilization of Colloid Mills

It has been claimed by the manufacturers of some colloid mills that their machines actually produce disintegration of solid particles. After a large number of experiments with various materials, the author is convinced that this is incorrect and that no colloid mill actually grinds or breaks down solid particles to any extent. What a colloid mill does accomplish is the deflocculation of particles, originally discrete, which have formed loose aggregates on packing. The colloid mill disperses these aggregates in the presence of a liquid, but

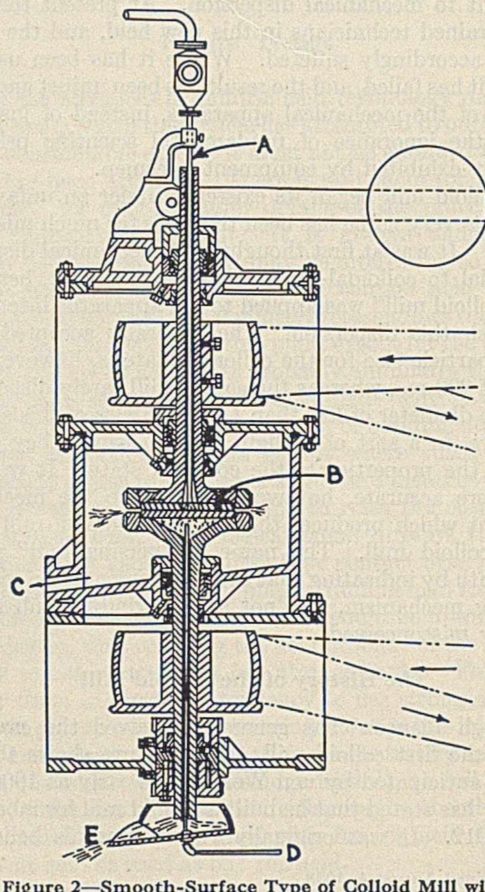

Figure 2—Smooth-Surface Type of Colloid Mill with Opposed-Disk Working Surfaces

A—Material inlet
B—Working surfaces
C—Material outlet
D—Cooling-water inlet
E—Cooling-water outlet

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[4] Auspitzer, Ind. Eng. Chem., 20, 413 (1928).

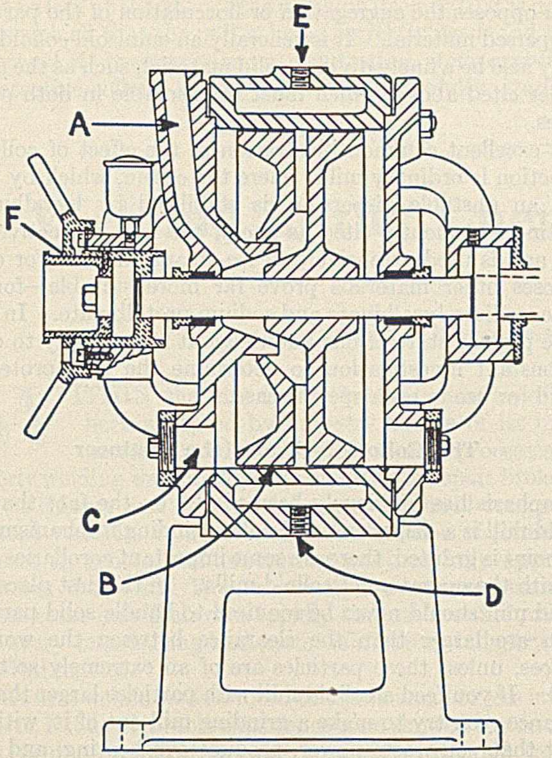

Figure 3—Smooth-Surface Type of Colloid Mill with Nearly Cylindrical Delayed-Action Working Surfaces

A—Material inlet
B—Working surfaces
C—Material outlet
D—Cooling-water inlet
E—Cooling-water outlet
F—Clearance adjustment

it does not disintegrate. To illustrate this point, we may take the example of zinc oxide. When this is first produced it is in a state of extreme subdivision, but when packed the fine particles group together in aggregates of various dimensions. These aggregates are easily dispersed again in the presence of oil by the action of the colloid mill, a large part of the action being the complete wetting of the individual particles by the oil so that they can no longer come in contact. The paint manufacturer generally considers this to be a fine grinding job, but it is really a quite different proposition.

The deflocculation of solid material, as described above, is one of the most important industrial applications of the colloid mill. Pigments such as chrome yellow, iron and zinc oxide, umber, and lampblack, for use in paints and enamels are treated with good economy and high capacity in these machines. Paints such as outside whites and flat whites can be prepared in a colloid mill at a rate of from 250 to 300 gallons per hour, a capacity far beyond that of the roller mill. Lacquers of high grade may be prepared by the colloid mill if a supercentrifugal clarifier is used following the mill to remove any relatively large particles not dispersed in the latter. Mica, clays, and dyes have also been treated with excellent results in the colloid mill.

Although the deflocculation of solid material is important, the application of colloid mills to emulsification processes is even more extended. Oils, resins, and waxes of all kinds are readily treated. Creams, sauces, blended extracts, and similar foodstuffs in general find the colloid mill an economical means of production. Milk is reconstituted in colloid mills from milk powder, sweet butter, and water. Fresh milk and ice-cream mixes are homogenized, and animal and vegetable fibers and tissues are subjected to efficient extraction processes. An interesting application of the colloid mill indirectly to the separation of materials is in the production of carbolic and cresylic acids from tar oils. The tar oils are first emulsified with water in a colloid mill. The emulsion is then broken and the carbolic and cresylic acids remain dissolved in the water phase.

Both the dispersion of solids and the production of emulsions depend for their success upon an accurate knowledge of the principles of colloid chemistry. Among the factors which exert particular influence in industrial work are hydrogen-ion concentration, temperature, and the utilization of protective colloids as stabilizing agents.

As a demonstration of the effect of hydrogen-ion concentration consider the specific case of a vegetable-oil emulsion, such as technical olive oil containing a small quantity of free oleic acid. If 0.25 per cent of gum karaya is added to the water phase and the technical olive oil is poured in slowly with rapid agitation, a fair emulsion will be formed, particularly if the material is passed through a colloid mill. This emulsion will not coalesce readily, but it is not so good as may be obtained. It will show a reading of, say, pH 4.7. If to this emulsion one adds sodium hydroxide solution until a pH of 8.0 is obtained, the emulsion shows a decided improvement. Now, if one continues to add sodium hydroxide, the effect is finally detrimental. On increasing the pH to 12.0, the emulsion will become less stable and less finely divided than when it was taken slightly over the neutral point with a pH reading of 8.0 or slightly greater. Microscopic examination will show the emulsion under this condition to be better than when the pH is either higher or lower.

The example above is given merely to indicate the importance of pH adjustment in the making of emulsions. Of course, with other types of emulsions and with different oils the necessary optimum pH varies over a considerable range. As a general rule, if one wishes to make emulsions of the oil-in-water type stable over long periods of time, the hydrogen-ion concentration should be adjusted slightly on the alkaline side. In industrial work accurate control of pH frequently means the difference between satisfactory emulsification and a worthless product.

Notwithstanding the importance of hydrogen-ion concentration in emulsification processes, it is the single factor most frequently neglected in practice. This has been due largely to the complicated apparatus required for its determination by electrical methods, and to the unsatisfactory results obtained by the use of colorimetric pH methods on turbid dispersions. Recently, however, a simple method for determining hydrogen-ion concentration in colloidal or semi-colloidal dispersions has been developed.[5] This method is sufficiently accurate for practical purposes and may be used with turbid suspensions as well as with clear solutions or dispersions. Even in the hands of an inexperienced person a reading may be obtained in less than two minutes.

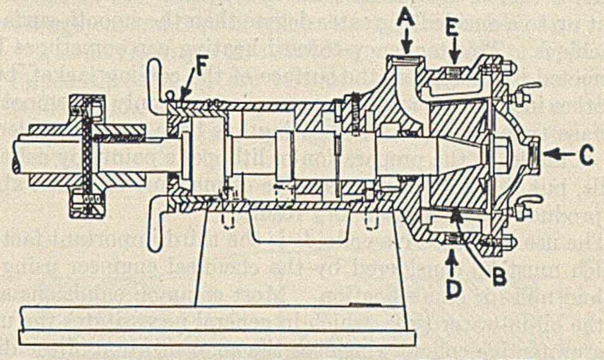

Figure 4—Roughened-Surface Type of Colloid Mill with Conical Grooved Working Surfaces

A—Material outlet
B—Working surfaces
C—Material inlet
D—Cooling-water inlet
E—Cooling-water outlet
F—Clearance adjustment

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[5] Travis, "Mechanochemistry and the Colloid Mill," Chemical Catalog Co., 1928.

Although hydrogen-ion concentration is the most important factor in many industrial processes, proper control of temperature is likewise of vital importance in the preparation of emulsions and dispersoids. For example, in cases where albumin is used as a stabilizing agent, the accidental attainment of a temperature of 90° C. in the colloid mill would cook the albumin and destroy its value as a stabilizer. The importance of temperature is also illustrated in the case of cod-liver oil emulsions made by the usual pharmaceutical methods, using gum tragacanth and acacia. If the temperature of the material passing through the colloid mill used for dispersion is allowed to exceed 35° C., the product is unstable and quite likely to separate into oil and water phases after short periods of standing. Some emulsions are also affected by the absorption of carbon dioxide from contact with the air, but this effect has been found to be negligible below 15° C. In each of the cases cited above, proper control of temperature is of fundamental importance.

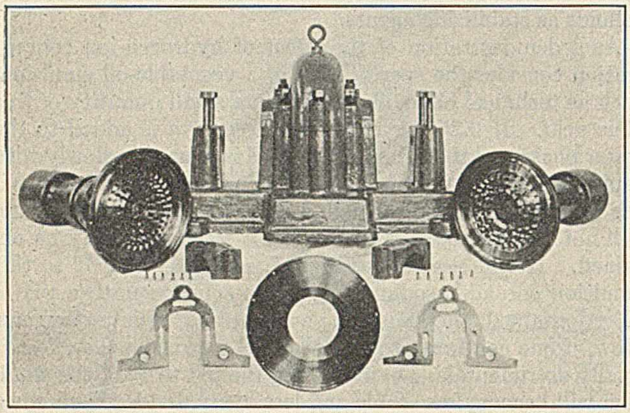

Figure 5—Roughened-Surface Type of Colloid Mill with Opposed-Disk Working Surfaces

The decrease in stability of many dispersions with increase in temperature sometimes limits the choice between various types of colloid mills or limits the rate at which a certain mill may be run for a certain process. In general, the more vigorous action of roughened-surface machines causes them to heat up to a decidedly greater degree than the smooth-surface machines. This tendency toward heating can sometimes be corrected by increasing the surface of the cooling jacket, but in other instances it may be necessary to use only the smooth-surface type of mill. Overheating has been a real problem, for example, in the preparation of lithopone paints by colloid mills, but the smooth-surface type of machine has been able to produce highly satisfactory results.

The use of protective colloids is the third important factor which must be considered by the chemical engineer using a colloid mill for emulsification. Most common emulsions are of the oil-in-water type, which in general necessitates the use of a protective colloid whenever the concentration of the dispersed phase exceeds 1.5 per cent, in order that the emulsion may be stable over long periods of time. Frequently, however, the material to be dispersed carries its own protective colloid. For example, the cocoa fat of chocolate emulsions is stabilized both by fine solid particles of cocoa powder and by proteins naturally present in the material. In many other cases it is imperative, however, that some material be added as an emulsifying agent to aid in the maintenance of the dispersion produced in the colloid mill. Some of the water-soluble colloids most used industrially are the sodium and potassium soaps; egg albumin, pectin, glue, and other proteins; gum arabic; Irish moss; starch; saponin and various bark extracts.

The protective colloid or stabilizing agent is a material which opposes the aggregation or flocculation of the particles of dispersed material. It is generally an emulsoid colloid, but it may also be a finely divided solid material, such as the cocoa powder cited above, which must be insoluble in both of the phases.

An excellent common illustration of the effect of colloidal protection is ordinary milk, where the casein, which by itself gives an unstable dispersion, is stabilized by lactalbumin. Gelatin is frequently cited as one of the best protective colloids and is used extensively in ice-cream mixes. For other purposes other materials prove far more suitable—for example, sodium lycalbinate and sodium protalbinate. In fact, in the present state of our knowledge it is necessary to carry on constant investigation to determine the best protective colloid for use in each specific case.

The Colloid Mill and the Engineer

Emphasis has previously been placed on the fact that the colloid mill is a dispersing and not a grinding mechanism. If this point is granted, there are some important corollaries dealing with the operation of colloid mills. In the first place, the colloid mill should never be required to handle solid particles which are larger than the clearance between the working surfaces, unless these particles are of an extremely soft material. If you feed a colloid mill with particles larger than its clearance, you try to make a grinding mill out of it, with the result that you waste power, produce overheating, and wear the working surfaces of the mill much more rapidly than if proper conditions were maintained. Solids which are to be dispersed in colloid mills should practically always have a preliminary grinding to 80 mesh or smaller, depending on the clearance used in the specific mill.

Together with the preliminary grinding of material, the mill itself should be operated at a clearance of from 0.006 to 0.008 inch in most cases, in spite of the claims made for some mills that they may be operated at a clearance of 0.002 inch. The actual clearance employed for any specific case depends largely upon the viscosity of the dispersing medium and the properties of the material to be dispersed. In some cases these factors may require much larger clearances than those quoted above.

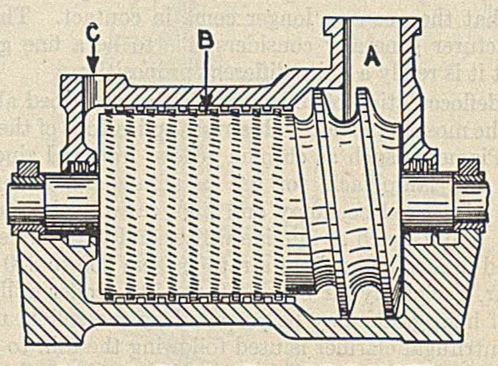

Figure 6—Turbine Type of Colloid Mill

A—Material inlet; *B*—Working surfaces; *C*—Material outlet

Because colloid mills are operated at speeds of 3600 r. p. m. or higher, there is inevitable wear on the working surfaces even when conditions are the best. Mills used for emulsification are naturally subject to less wear than those used for the dispersion of solids, but in all cases wear does occur. Mills which allow, first, for the adjustment of the clearance to compensate for wear, and finally for the ready replacement of the working surfaces, enjoy an advantage over mills not so advantageously designed.

Unsatisfactory results obtained with a colloid mill should not be laid at the door of the machine itself until it is definitely determined that the mill is being correctly used, and that the factors of hydrogen-ion concentration, temperature, and protective-colloid action have been carefully studied. It should be reiterated in conclusion that the mechanism is only one-fifth of the problem and the knowledge and correct application of physical chemistry is the important four-fifths of the utilization of the colloid mill.

Welding in the Chemical and Process Industries[1]

W. Spraragen

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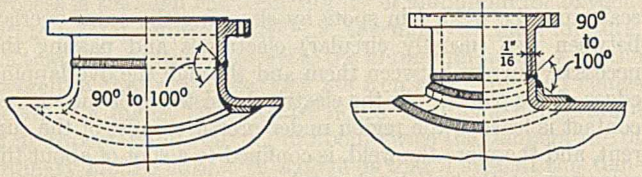
Within the last ten or twelve years welding has been accepted by industry as one of its most important production and repair processes. Formerly welding was employed principally to repair broken parts of machinery and other metal parts, but until comparatively recent years its value as a standard method of joining metal pieces in general manufacturing was not fully appreciated. During the World War, however, the various welding processes came into their own rapidly because speed of production in every metal-using and metal-fabricating industry became a vital matter.

At first welding was limited to use on small or less important parts, but as favorable experience soon showed the desirability its field of application was gradually extended to heavier and more important construction and repair work. Many practical demonstrations of the utility of welding focused attention on its marked economic advantages, with the result that now all welding processes are widely used in all branches of manufacturing. Welding is employed for an almost limitless number of applications, from the manufacture of such small articles as watch stems to the largest metal-fabricated structures—ships, locomotives, trunk oil and gas pipe lines, gas tanks, and the largest turbine electric generators.



Design of Flued Outlets with Reinforcing Pads Oxyacetylene Welded

Before considering the applications of welding a brief description will be given of the various methods by which it is accomplished. This will be followed by a discussion of the fundamentals of welding which are more or less common to all its applications in important construction work, and finally with problems that are peculiar to the chemical and process industries.

Welding Processes

Forge Welding—Until about forty years ago this was the only available method, and it has been in use to some extent for centuries. After properly shaping the two surfaces to be joined, the parts are heated to welding temperature in a forge or furnace and then hammered, rolled, or pressed together, usually with the aid of some fluxing material.

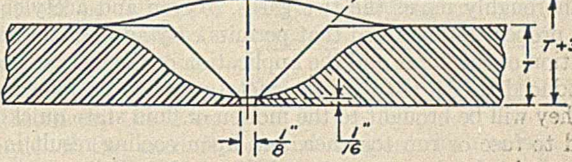
Arc Welding—There are several divisions in this method, as will be indicated below. Several of these divisions may be further subdivided as to whether the current is direct or alternating and whether the operation is manual, semi-automatic, or automatic.

Metal Arc Welding with Bare Electrodes. In this method an arc is struck between the wire or rod of suitable composition, called the electrode, and the parts to be welded. The parts to be joined are made one side of an electric circuit, the other being the electrode. The parts to be welded should be properly shaped and are usually beveled on both edges in the case of plates to be joined in the same plane by a "butt" weld. The metal is fused at both ends of the arc and the fused electrode deposited in the joint until the latter is properly filled. The power is usually supplied by a suitable transformer or by an arc-welding generator which delivers an open-circuit voltage ranging from 35 to 75 volts. The arc should be as short as possible in order to avoid oxidation of the metal and the inclusion of harmful gases and to secure the proper penetration.

Metal Arc Welding with Coated Electrodes. These have been used in some form almost from the beginning of arc welding. In general, the coatings serve as a fluxing or deoxidizing medium, or provide a protective vapor around the arc.

Arc Welding in a Reducing Flame. In this method a cylindrical jet of gas surrounds the electrode and burns around the arc. Pure hydrogen, water gas, alcohol vapor, and a number of other gas combinations have been tried with considerable success. These welds are, in general, superior to the bare electrode welds, particularly as regards ductility. The reducing flame generally serves the same purpose as the electrode coatings and apparently with somewhat better results, although this method is still in the experimental stage.

Atomic Hydrogen Arc Welding. A fine jet of hydrogen is forced through an arc formed between two tungsten electrodes. The high temperature of the arc breaks up the hydrogen molecules into hydrogen atoms, which recombine into molecules after passing through the arc, giving up the heat absorbed during dissociation in the arc. The welding wire is fused in this flame and deposited in the joint exactly as in the case of gas welding, described elsewhere. The intensely reducing character of this hydrogen flame results in a nearly perfect weld.



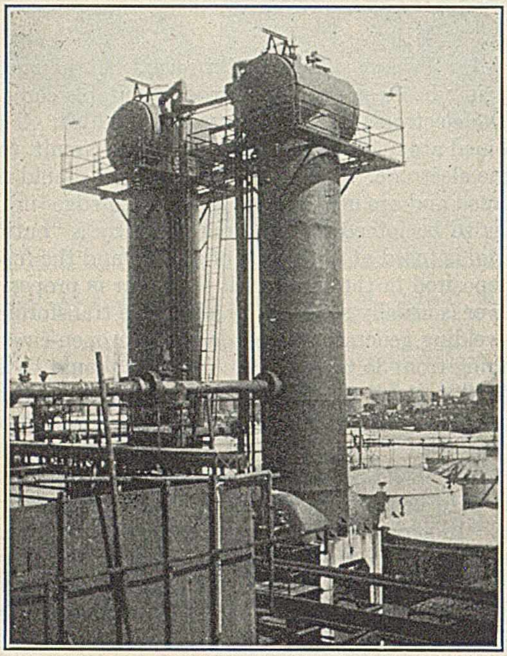
Making a Butt Weld in Pipe

Carbon Arc Welding. In this method, invented in 1881, an arc is struck between a carbon (or graphite) electrode and the parts to be welded. The welding wire is then fed into the arc and fused into the joint. For hand operation this

[1] Received March 5, 1929.

requires two hands as in the case of gas welding or atomic hydrogen arc welding. In fact, it differs from gas welding only in the source of the heat, the gas flame being replaced by the arc. In some cases the welding rod is laid in the joint groove and the carbon arc passed slowly along the joint until the fusion is complete.

Electronic Tornado Welding. This name is applied to a magnetically controlled carbon arc which produces welds with good ductility. Oxidation is largely prevented in this process. Great speeds are possible, although the application is limited to "downward" welding.



Fractionating Tower in Petroleum Refinery with Oxyacetylene-Welded Joints Evident through Insulation

Gas Welding—This process of fusion welding is generally carried out by the heat produced by the burning of acetylene in the presence of commercially pure oxygen, the flame temperature so attained being probably about 5500° F., which, in view of the concentrated flame, is high enough to melt any metal locally, and so allows pieces to be easily fused together. It is necessary, when welding thick materials, to bevel the edges to be joined so they form a V, which is filled up by melting into it a rod of suitable composition, the weld metal also being fused to the base metal.

Torch. An oxyacetylene welding torch is an instrument that thoroughly mixes the two gases, oxygen and acetylene, in the proper amounts and that permits easy adjustment and regulation of the flame and the application of the intense heat so produced to the edges of the metal parts to be joined so that they will be brought to the molten or fluid state quickly, caused to fuse or run together, and upon cooling result in a joint or union having strength and chemical qualities approximately the same as those of the original parts. The welder requires a small flame and little heat for welding thin-gage metals and a large flame and much heat when welding heavy sections. This is the reason for the separable interchangeable tips furnished by the torch manufacturers in several sizes ranging from the smallest to the largest practicable to use.

Resistance Welding—In this method, invented about forty years ago by Elihu Thomson, the parts to be joined, after proper shaping, are pressed together. A large current is then passed through the joint until it has reached welding temperature, when further pressure is applied, upsetting the joint and completing the weld.

As the electrical resistance of the contact surface is much greater than that of the solid metal, most of the heat is generated at the joint surface where it is desired. The larger the current the more rapid the heating, the less the heat extends back from the joint into the metal, and the less the upset.

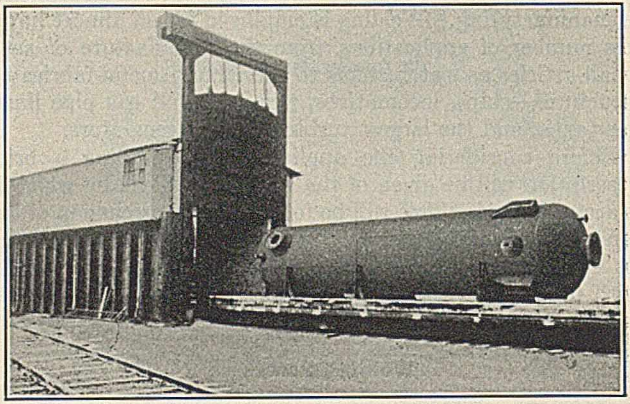
The voltage required is so low and the current so high that the only convenient source is an alternating-current transformer built into the welder and as close as possible to the jaws which hold the parts and transmit the current to them.

Butt Welding. The simple type of resistance welding described above is usually known as butt welding, and has been applied to join sections of widely varying shapes up to 36 square inches in section.

Parts to be welded are clamped in dies of welding machine giving equal or nearly equal projections to both parts, the primary circuit closed, and the ends of parts brought together slowly. When these ends actually touch each other, they will "flash"—that is, minute particles of molten metal will fly off; this flashing is continued until the entire faces of abutting ends have reached a welding heat, when rapid and heavy pressure is applied, forcing ends together and completing weld, at the same time opening primary circuit. The above is, without doubt, the preferred method of welding, as the power and time consumption is considerably less and the personal equation of the operator enters to a much less degree than in any other type of weld, thus producing more uniform results.

Spot Welding. Where air-tightness is not required, a lap seam may be welded in spots by clamping the seam overlap between two (usually circular) electrodes and passing the necessary current between them and through the overlapping edges of the plates. As the electrical resistance of the surface contact is least in the region under pressure, most of the current, and therefore the weld, is confined to a spot of about the same area as that of the electrodes.

For relatively thin metal this method is much more rapid and economical than any other known method of making a joint where mechanical strength alone is required. The mechanical strength obviously depends upon the number and size of the spots. With a double row of staggered spots it is easy to make the joint strength equal to that of the sheets themselves.

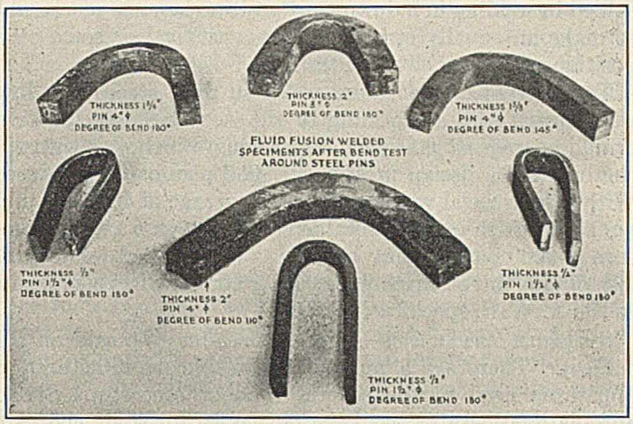


Welded Pressure Still Coming Out of Annealing Furnace

Still, 7 feet 7 inches in diameter, 33 feet 2 inches long
Thickness of plate sheet, $4^1/_2$ inches
Thickness of elliptical heads, $4^5/_8$ inches
Weight, 89.5 tons
Tested to 1580 pounds

Seam Welding. The overlapping edges of sheet metal are passed between two narrow roller electrodes, the speed, current, and pressure being so adjusted as to produce a continuous seam weld. This method is usually limited to relatively thin sheets, but is readily applicable to either straight seams or to circular seams as for the flanged heads of cylinders. The employment of this method for the manufacture of barrels, moderate-sized transformer tanks, and numerous other similar containers has resulted in a very large saving in cost. Thousands of such welded containers are made every day.

ALUMINO-THERMIC (THERMIT) WELDING—Thermit is a trade name for a mixture of finely divided aluminum and iron oxide, which when ignited reacts to produce a superheated liquid steel at 5000° F. The underlying principle of this process is the high chemical affinity of aluminum for oxygen. Up to a temperature of 2800° F. thermit is an inert mixture. At that temperature, however, the aluminum unites with the oxygen of the iron oxide, and the iron is set free and comes down as a highly superheated liquid steel at a temperature of approximately 5000° F., or about twice the temperature of ordinary molten steel. It is obvious that if steel at this temperature is poured around the sections to be united, especially if the sections have previously been preheated to a bright red heat, it will melt those sections and amalgamate with them so that the whole will cool to form a single homogeneous mass or, in other words, a fusion weld.



Samples Welded by Fluid Fusion Process

Fundamental Elements of Welding

SELECTION OF PROPER MATERIALS—The selection of suitable materials is important in the application of welding to any industry, but is increasingly important in the chemical industry because we must have in mind the requirements of the specific application and we must have a material in which we can produce a sound, dependable weld. For example, in order to withstand the corrosive effect of acid or alkali solutions we would perhaps consider one of the newly developed corrosion-resisting alloys. Some of these corrosion-resisting alloys are more readily weldable than others. In some cases where the corrosion-resisting property is dependent on special heat treatments, excellent welds can be produced from the standpoint of mechanical strength, but the welds may not be able to withstand the corrosive action involved unless they are given special heat treatments or made in special ways. The economics of the situation must also be carefully considered, because it may be preferable to use thicker sections of low-carbon steel even though this steel may be less resistant to corrosive action, because it is cheaper, more readily weldable, and owing to the thicker section will last as long as vessels made from some more expensive alloy. The considerations given above apply in some cases with equal force to vessels that must resist elevated temperatures or vibratory stresses or a combination of these. For example, it has been found in the oil-cracking industry that the best steels are the plain carbon steels, because the strength increase obtained in using the ordinary alloy steels at elevated temperatures is not sufficient to cover the higher costs of the steel and increased costs in fabrication. The advantages gained in corrosion resistance for such alloy steels do not become apparent until very expensive alloys are used. Some of these have very high chromium content, which have the disadvantage of becoming exceedingly brittle at the high temperatures involved. In some alloy steels, however, this difficulty of brittleness is overcome by certain additions of nickel. In some cases ordinary carbon steels are coated electrically with a deposit of chromium or with inert siliceous materials.

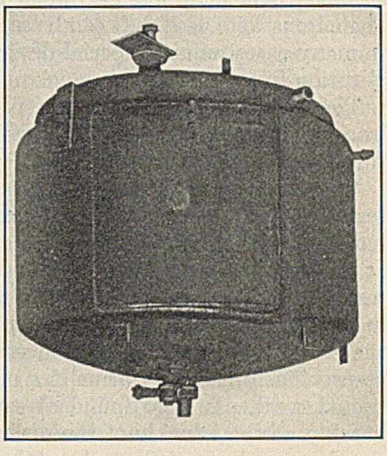
The problems of a suitable material therefore possess a great deal of ramification and can only be considered in detail for specific applications.

The selection of a suitable welding rod is equally as important, for the resultant welds are expected to have certain chemical and physical properties. Specifications have been prepared by the American Welding Society for welding ordinary materials. Special wires, however, may in some instances give better results.

All materials are suitable for welding, although by special technic and welding wire difficulties at first considered insurmountable may sometimes be overcome. Low-carbon steels and a great many alloys as well as non-ferrous metals can be satisfactorily welded by one or more of the fusion welding processes.

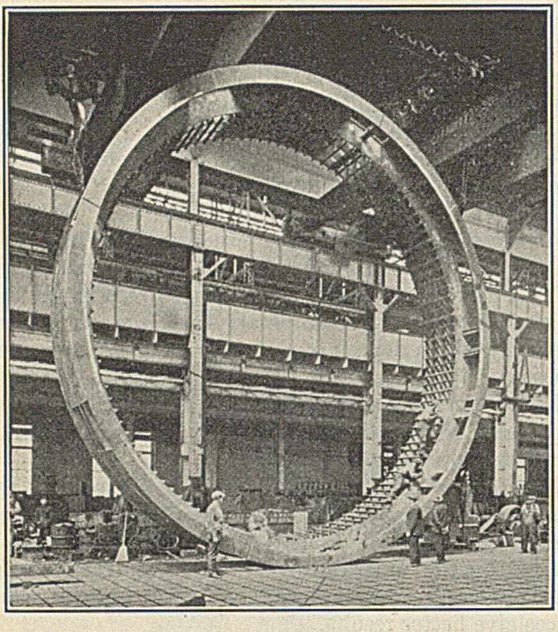
It is generally agreed that a carbon content of not over 0.25 per cent lends itself most readily to welding. The greater ductility of this material minimizes distortion and the development of local stresses due to the heat of welding. Steel plate of fire-box quality should be specified for all important work. This steel is generally free from impurities of various kinds that are harmful to welding. Defects in steel plates, such as segregations and laminations, must be avoided.

PROPER DESIGN—It is a wrong basic principle to substitute welding for riveting in a structure originally designed for riveting. Although such a course can sometimes be justified as a temporary expedient, it is not fair to judge welding from results obtained in such cases. The structures that will be fabricated by welding should be designed with full recognition of these circumstances. As an example of the need for special designs which recognize the fundamentally different bases of the two methods of joining metals, it may be noted that, whereas for riveted joints it is necessary to overlap the plates or employ straps, the use of welding often permits butt joints to be used. This effects a considerable saving beyond that which could be made if the overlap necessary with riveting were retained.



Portion of Jacket Had Been Removed to Repair Inner Lining

The Carnegie Institute of Technology has made some tests for the Westinghouse Electric and Manufacturing Company in order to determine the various types of connections required in the steel frames of buildings to be fabricated by arc welding, among which are some comparative tests on three specimens,



Welding Stator Frame of 40,000-kw. Generator for Conowingo Power Development, Built by the General Electric Company

fabricated as girders on comparable materials. The results were as follows:

	Length	Weight	Yield at:	Ultimate Stress at Failure
	Feet	*Pounds*	*Pounds*	*Pounds*
Riveted girder	15	798	55,000	68,900
Welded girder of riveted design	15	785	65,000	77,200
Welded girder of welded design	15	795	60,000	110,350

The girder designed especially for welding was made up entirely of flat plates. A suitable web plate was welded to two flange plates with small flat plates used as stiffeners and a suitable cover plate was also welded to the flange plate. No angle irons were used. It can be seen, therefore, that welding in many cases requires special designs and not merely a substitution in a riveted design.

The use of clip angles, gusset plates, brackets, and angle iron may sometimes be eliminated entirely in welded structures.

Vessels made with riveted joints cannot be satisfactorily tested at hydrostatic pressures exceeding about one and one-half times the working pressure because of the serious leakage at the joint. The welded joint, on the other hand, may be tested up to its breaking point. In experiments carried out in the laboratories of one or two companies, it was found that there were several weak spots in vessels fabricated according to previously accepted principles of design. Zones of unexpected weakness were found at several important points—notably at the knuckle of the dished heads, at the manhole openings, and at nozzles. Investigations show that the correct design for eliminating high local stresses is an ellipsoid with a ratio of 2 to 1 between the major and minor axes.

Design fiber stresses of 8000 to 9000 pounds may be used if qualified welders are available. The higher figure should only be used with special materials or methods. Where the size of the vessel permits, it is desirable to construct the shell in one course. Where girth seams are necessary, the longitudinal welds should be staggered an equal number of degrees. Several approved methods have been developed for welding nozzles and nipples. An unreënforced manhole opening decreases the strength of a thick-walled vessel by 40 per cent. The minimum thickness of head should be at least equal to the thickness of the cylinder.

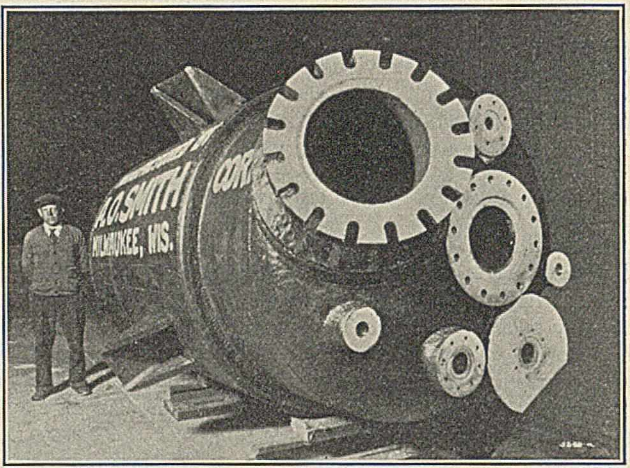
An ordinary dished head requires a thickness about one and one-half times the thickness of the main cylinder in order to approximate the strength of the vessel cylinder. This is a disadvantage because of the stress effect of the joint between the plating and the thicker head.

QUALIFIED WELDERS—It is now generally recognized that on important work only qualified welding operators should be used. It is not sufficient to judge a man by experience alone, but he must be required to make up test coupons using the same materials and thicknesses that he will be called upon to weld in service. A skilled operator on thin work may not be able to do satisfactory work on thicker materials, or if he is skilled in welding in a downward position he may not be able to make an equally strong weld in a vertical or some other position without additional training.

Test coupons taken from welds in mild steel made by a welder with wire conforming to the A. W. S. specifications should average 45,000 pounds per square inch and with this combination a design pressure of 8000 pounds may be used. With some special welding wires an average of 50,000 pounds per square inch may be obtained, in which case a design pressure of 9000 pounds may be used. Very skilled welders can also obtain this strength with good grades of wires conforming to the A. W. S. specifications.

SUITABLE APPARATUS—A great deal may be said on this subject. There are a number of reliable manufacturers of apparatus used in the several welding processes. Special automatic apparatus has been developed for some classes of work. Other methods and technic are designed to give welds of extreme ductility. Manufacturers who contemplate the use of welding should make a thorough study of this phase and adopt types of apparatus most suitable for their specific needs.

PROPER TECHNIC—Proper welding technic should be developed after the most careful study by competent experts. In complicated structures, by the adoption of a suitable order of welding, trouble due to stresses and distortions may often be completely avoided. Number of layers, use of jigs, proper current, proper-sized tips, gas pressures, methods of assembling the work are all important factors which may determine the success or failure of a specific application. In general, except for automatic work the longitudinal seam should be of a double-V construction, the outer V being welded first. Before welding the inner V, burrs, globules, or oxide formations should be removed by a chisel. It is recognized that



Jacketed Autoclave of 800 Gallon Capacity for Process Industries, Welded by the A. O. Smith Corporation

Inside diameter 54 inches, over-all length 11 feet, inner body 3 inches in thickness and the jacket 2 inches. The weight is approximately 35,000 pounds and the vessel is made to operate at from 600 to 900 pounds pressure while heated by means of live steam in the jacket.

for heavy vessels 1 inch in thickness or over it is desirable to anneal the structure. This is not necessary on thinner walled vessels.

Competent Supervision and Inspection—There must be a competent supervising and inspecting force to see that all the elements which enter into the making of a successful weld are carried out. This involves inspection of the material and its preparation for welding. For example, the edges must be free and clean from dirt, oil, or grease. Inspectors must also see that the proper currents or gas pressures are employed and that all the details entering into the correct technic of welding are carefully followed.

Testing of the Finished Product—It is customary to test the welded vessel hydrostatically to three times the working pressure with the application of a hammer test at one and one-half times the working pressure. Exact procedure has been worked out for the weight of the hammer and method of application of the test.

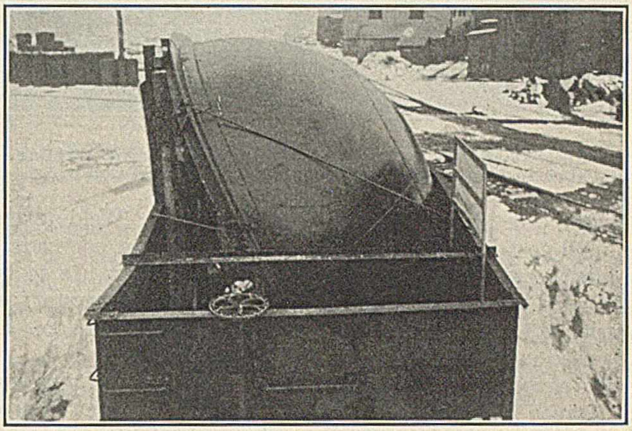
Specific Requirements of Chemical Industry

Reliability of Welds—Reliability of welds is important in construction work, where failure might result in loss of life or property. If all the elements enumerated above that enter into the making of a successful weld are closely followed, the variation of the finished product should be no greater (perhaps less) than with other methods of fabrication. Only experienced welding engineers should be responsible for the design and selection of materials and apparatus. Qualified welders and competent inspectors and supervisory force should be used.

There are in existence today hundreds of vessels which are called upon to withstand the most drastic service conditions. Some are operating at extremely high temperatures at heavy pressures. Other vessels are undergoing constant reversal of stresses. Vessels made by reliable companies have withstood these tests and are in daily commercial use, as will be indicated by a number of the illustrations.

High Temperatures and Pressures—Some chemical processes depend upon their success for high temperatures and pressures. Without the aid of welding it has been difficult and sometimes impossible to construct vessels that are able to meet these very severe requirements. For example, it has become recognized that 900° F. is a temperature around which oil-cracking operations can economically be carried out. The butt joint is generally considered the best for this class of work, which can, of course, be readily made by one or more of the fusion welding processes but not so readily by other methods of fabrication. At first great fears were expressed that the welds would not be able to withstand these high temperatures. Preliminary short-time investigations, made under the auspices of the American Bureau of Welding, indicated that good arc and gas welds follow very closely the properties of fire-box steel from room temperature to 1000° F. There seemed to be a gradual increase in strength in both the parent metal and the welded joint up to about 600° F., with a rapid falling off in strength after that temperature, so that at 1000° F. the strength of the joint and of the parent metal was about half of that at room temperature. Long-time tests have not yet been made by the Society, but other experimenters have found that at high temperatures the falling off in strength of welded joints will be about the same as that of the low-carbon steels. In some tests reported by these investigators the decrease in strength at about 900° F. in long-time tests was to 25 per cent of the ultimate strength at room temperatures. There are hundreds of welded vessels made by one company alone for oil-cracking, which requires both high temperatures and pressures.

Corrosion-Resisting Properties—It has been said that a bibliography of articles on corrosion would occupy a good-sized volume in itself. Problems involving corrosion must be studied individually. It is possible to weld most of the corrosion-resisting alloys satisfactorily, although special technic and materials are sometimes needed. Welding apparently has the advantage as a method of fabrication in most applications involving corrosion. The problem is somewhat complicated if temperatures and repeated stresses are involved, as high temperatures in many instances increase the rate of corrosion, whereas corrosion often lowers the endurance limit. As pointed out elsewhere in this article, it is sometimes advantageous to use ordinary carbon steels with a deposit of chromium. This is sometimes done in the oil-cracking industry.



225-Ton Kettle, Fabricated by Petroleum Iron Works
14 feet inside diameter by 6 feet 9 inches deep. Thickness of plate, 1¼ inches. Weight, 11.3 tons fire-box steel.

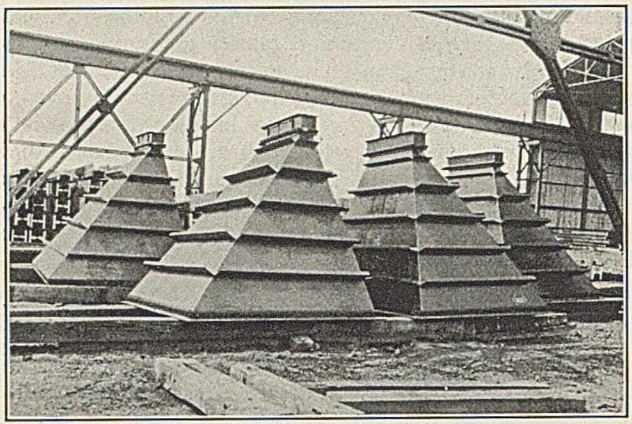
Endurance Limit—The endurance limit of materials is often affected by corrosion and temperature. Where these factors are not involved, the endurance limit of welds made in ordinary steels may be taken at about 18,000 to 20,000 pounds. It is customary to use these figures with a design factor of safety of two. Several companies, however, claim to have been able to produce welds with an endurance limit as high as the parent metals themselves, although these are special cases and in general these welds are quite superior in ductility, soundness, and microstructure.

Piping—A piping system cannot be purchased all ready to install like a piece of machinery, but it must be fabricated in place. Lengths must be cut and connected to obtain a continuous line and outlets for branches and connections provided.

Innumerable tests demonstrate that a properly welded joint is as strong as the pipe wall itself and to all intents and purposes becomes an integral part of the pipe. Therefore, the joint will last without maintenance as long as the pipe. Thus, on account of the strength of the joint, higher pressures may be safely carried than would be permissible with screwed, flanged, or any other type of joint. Owing to its great tensile strength it is largely able to resist expansion and contraction stresses caused by changes in temperature.

Economies effected by welding are not limited to the making of the joint itself, but begin at the pipe mill and extend beyond the installation, continuing throughout the entire life of the line. Savings due to welding of pipe start at the mill. Most mills formerly made pipe of approximately 20-foot lengths to facilitate handling, cutting, and threading. They are now responding to public demand and manufacturing pipe in 40-foot lengths, because welding has made it possible to take advantage of the obvious economies of using the longer lengths.

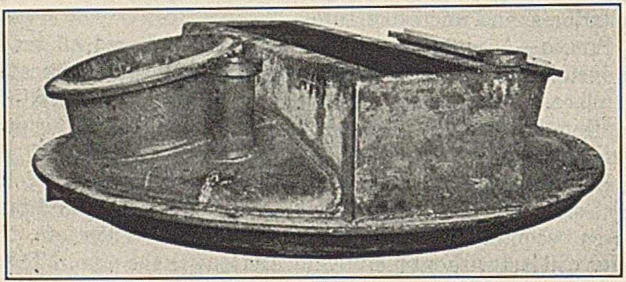
Any special fitting can be fabricated by cutting with a torch and welding with the torch or arc right on the job. No thought on the part of the designer need be given connections between pipe lines if the pipe is to be welded. Welding can be used to advantage whether the job is to be completely welded or whether only specials such as headers are to be fabricated by this process. There are no delays necessary in waiting for special fittings. No special expensive tools or dies used in threading are needed.



Rivetless Steel Hoppers Completely Fabricated by Arc Welding. Fabricated by Mississippi Valley Structural Steel Company

The covering contractor will cover or lag a welded pipe line for a much lower price than he will an identical screwed pipe line, as the former does not require molded fittings. The finished job is also more efficient. The American Society of Heating and Ventilating Engineers recently conducted an investigation to determine the efficiency of pipe coverings. Their tests indicated that a pipe line with bare flanges, but insulated along the body of the pipe, loses half as much heat as a completely uninsulated line.

Circulation of gases or liquids through a welded pipe line is maintained with less friction than when fittings are used. Operating experience in pipe-line work has shown that welded lines have somewhat greater carrying capacity than other types of the same diameter, and the reason may be traced directly to reduced friction of the flow. The factor of flow resistance becomes increasingly important as pipe size decreases.



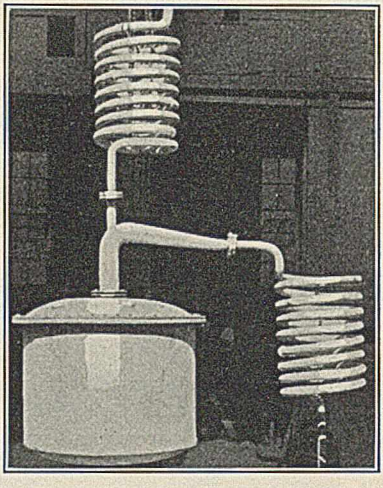
Welded Structural Steel Top Frame for 73,000-Volt Oil Circuit Breaker

A further advantage of welded construction is evident when it is desired to make changes in an existing line, to add a new outlet, or to extend the line to another department. Where the line can be conveniently shut down for a few minutes, a new branch connection is made simply by cutting a hole in the main line with the cutting blowpipe and the welding in a short length of pipe carrying a shut-off valve. As soon as welding is finished, service may be resumed on the main line. There is thus a minimum loss of service. Perhaps of even greater importance is the improved service which such procedure allows the contractor to give. If all piping must be fabricated to exact length, as is the case unless welding on the job is done, it means that measurements for a portion of the piping at least cannot be taken unless the apparatus, such as boilers, turbine, and auxiliaries are in place and lined up. It is then necessary to order these materials, get them fabricated, and ship them often at an extra added expense and with consequent actual delay in time of starting of the pipe plant.

For the high-pressure and high-temperature lines where cast-steel fittings are usually required, another element which has an important bearing on service enters into the proposition. The manufacture of steel fittings and cast-steel headers is a somewhat speculative undertaking. The several fittings and headers of this kind required for a given job may be ordered weeks and sometimes months in advance. When finally cast there is always the possibility that one or more castings will be found defective and will tie up the entire job. Defects in the casting may not become apparent until machine operations are well along and often such defects do not show up until after the material is completely installed and tested. This feature often results in the discovering of defective material at the last moment with delays caused by reorders and remanufacturing running to weeks and months.

The methods of welding of pipes and fittings have now become standardized. Exact technic has been developed for making joints, templets have been prepared for fabricating connections, and jigs have been worked out for facilitating welding.

PRESSURE VESSELS—There is no application of welding that requires more complete control and closer adherence to the fundamental principles of welding than does the welding of pressure vessels. It can now be said that vessels of almost any thickness of materials commercially required can be satisfactorily welded although, of course, materials more than $1^{1}/_{2}$ inches thick as yet require special processes.



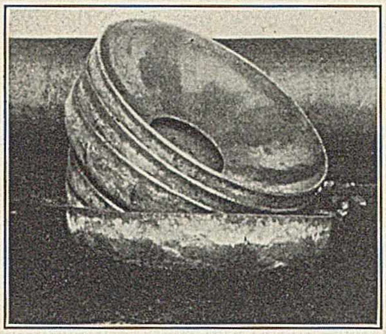
Oxyacetylene-Welded Stills of Non-Ferrous Metal

Within the last few years more than two hundred pressure vessels, ranging in diameter from 3 to 8 feet having wall thicknesses up to $1^{1}/_{4}$ inches, and carrying working pressures up to 300 pounds per square inch, have been oxyacetylene-welded under the supervision of one company alone and have proved entirely satisfactory under service conditions.

Another company, which has developed a special technic and method for arc-welding oil-cracking stills and other high-pressure vessels, has built seven hundred vessels using 45,000 tons of plate averaging close to 3 inches in thickness. This process is a fusion operation in a reducing atmosphere, which completely eliminates oxide inclusions and other impurities from the weld, leaving a metal of greater refinement than that of the plates joined. This company states that test bars, machined out of the deposited metal in a weld joining 0.20–0.30 carbon steel plates, have regularly given the following results:

Ultimate tensile strength	66,000 pounds per square inch
Elastic limit	50,000 pounds per square inch
Elongation	27 per cent
Reduction in area	53 per cent

Endurance tests reported by this company on joining 0.20–0.30 carbon-steel plates showed the endurance limit of the deposited metal to be at least 10 per cent above that of the plate material. The metal immediately adjacent to the weld showed an improvement of about 4 per cent, and at no point was there any decrease in the endurance limit, below the value given for the plate itself.



Ellipsoidal Heads

Still a third company, using special technic in welding, covered electrodes of large diameter with special alloys, peening each layer, employing heavy currents, and keeping the metal in a molten state for an appreciable length of time has satisfactorily demonstrated its ability to build vessels of almost any commercial size or thickness. The physical properties of the welded joints approximate those given above. Both of these companies anneal the vessel after its completion. It should be noted that these are special methods and the ordinary arc welds made by hand operators do not possess these desirable characteristics. Several methods are, however, available for commercial use that give welds of good ductility.

Particular attention is called to the desirability of the use of the double-V weld for the longitudinal seams and the design of head mentioned elsewhere. Careful and rigid procedure has been worked out for the exact technic to be followed in the fabrication of vessels by gas and arc welding.

Welding in Maintenance and Repair

Welding probably received its first impetus in repair and maintenance work in railroad shops. The several welding processes are annually saving the railroads of the United States millions of dollars. Almost every modern industrial plant of large size is now equipped to do its own repair and maintenance work.

The cost of routine maintenance and repairs can be substantially reduced by the intelligent use of welding and cutting. Innumerable cast-iron and steel parts, including large castings, which so often are scrapped, can be recovered, and in many instances welded right in place in the machine at a very small fraction of the original installation cost. In the emergency job, welding and cutting equipment in the hands of a competent man can do work in minutes which would necessitate delays of weeks if new repair parts were not available.

In repair work the welding engineer does not have the option of selecting materials best suited, but he must do his best on the "job" at hand. Almost all metals and their alloys can now be satisfactorily welded, but each requires its own technic. Some repair jobs call for gas welding, others for arc, still others of large sections for thermit welding, and sometimes in repetitive work for resistance welding.

Phenol Recovery and Treatment Works of the Hamilton Coke and Iron Company[1]

B. F. Hatch[2]

State of Ohio Department of Health, Columbus, Ohio

For the past five years the attention of administrative authorities has been constantly directed toward elimination of tastes and odors in public water supplies caused by phenol or other tar acids produced in the destructive distillation of coal. During this period unceasing effort to solve this troublesome problem has been made by the by-product coke industry in coöperation with health officials. Various methods of recovery and treatment have been attempted and, although a large measure of success has attended the efforts to protect public water supplies, the result has been accomplished at great cost in some instances and an operating burden of considerable magnitude has been placed on the industry as a whole. Consequently new methods of handling the problem are of especial interest to both health authorities and coke-plant officials. For this reason we present this paper describing the phenol recovery and treatment works recently placed in operation by the Koppers Company at the by-product coke plant of the Hamilton Coke and Iron Company, of Hamilton, Ohio.

Since the Koppers Company is fully protecting this process and apparatus by patents and further information may be obtained from that organization, no attempt will be made to explain minute details of design, but rather the information set forth at this time will be of general nature and as nontechnical as possible.

This phenol recovery system has already excited considerable interest and inspections of it have been made by representatives of a large number of by-product coke companies. In addition, the works has been visited by the chief engineers of the departments of health of West Virginia and Indiana in company with the chief engineer and the writer of the Ohio Department of Health. On these inspection trips information regarding the coke plant and the phenol recovery works has been given by J. T. Whiting, general manager of the Hamilton Coke and Iron Company, C. L. Haldeman, superintendent of the coke plant, and J. A. Shaw, research chemist of the Koppers Company. The coöperation and courtesy of these gentlemen in arranging for the inspection trips and in giving detailed information with regard to the coke plant and the phenol recovery process are gratefully acknowledged.

Location of Coke Plant

The blast furnace and by-product coke plant of the Hamilton Coke and Iron Company are located about 4 miles north of Hamilton, Ohio, on the west bank of Miami River. This stream is one of the larger tributaries of Ohio River and joins it about 30 miles southwest of the coke plant. Phenolic wastes from this plant, if discharged to Miami River, would first affect the water supplies of two small municipalities in Indiana which are situated on Ohio River close to the Ohio-Indiana boundary line, then that of Louisville, Ky., and other cities farther downstream.

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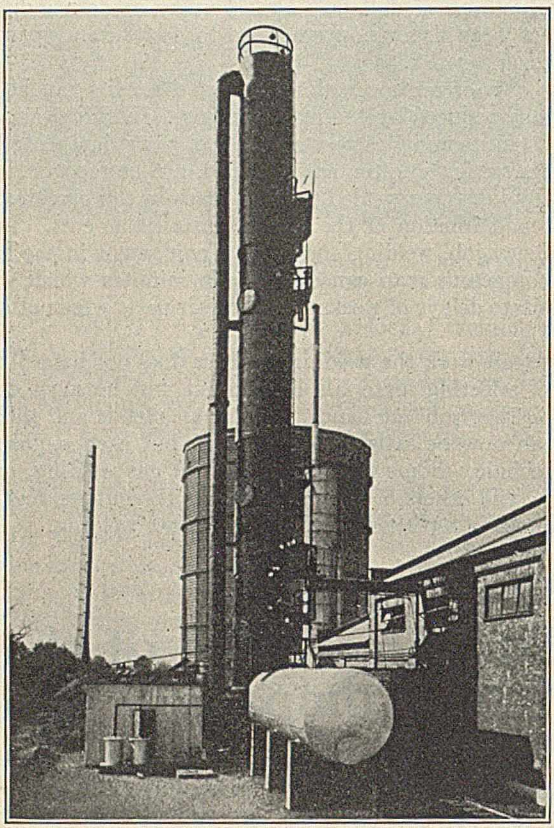
[1] Received February 16, 1929.

[2] Assistant engineer in charge Stream Pollution and Industrial Waste Investigations.

Description of Coke Plant

This coke plant is of the Koppers type and was placed in operation in April, 1928. The plant has 45 ovens 14 to 16 inches in width with a rated capacity of 1200 tons of coal coked per 24 hours. At the present operating schedule 1175 tons of coal are coked per 24 hours with a coking time of about 13$^1/_2$ hours. Ammonia is recovered by the direct process as ammonium sulfate. The light oils are refined to produce motor benzene and the heavy tars are sold as such. The gas after the by-products have been extracted is purified and sold to a distributing company for domestic consumption. The coke produced is sold principally for domestic and foundry use, although sufficient furnace coke for the local plant is manufactured.



Dephenolizing Apparatus, Hamilton Coke and Iron Co., Hamilton, Ohio

The weak liquor condensate is returned to the hydraulic main for flushing purposes at a temperature of about 76° C. At present the draw-off from the weak-liquor storage tank to the ammonia still amounts to from 15 to 20 gallons per ton of coal coked per 24 hours. The volume of waste water from the ammonia still at this plant will be accurately determined by weir measurements, but probably amounts to about 30 gallons per ton of coal coked or 35,000 gallons per day. The volume of waste water from the benzene plant is probably less than 5000 gallons per day. Thus far under normal conditions there has been no draw-off from the final cooler recirculation system. In fact, owing to evaporation which occurs in the cooling tower, it has been necessary to add some make-up water to this system. The plant water supply is pumped from a group of wells located adjacent to the plant and normally is at a temperature of 12° C.

Originally the sewer system for the coke plant was laid out and constructed in such a manner that all phenol-contaminated waste water could be diverted to a sump near the quenching tower and used for coke quenching. This plan was later modified by the construction of a phenol recovery works and the diversion of the dephenolized ammonia still wastes, the benzene plant wastes, and any excess water from the recirculation system of the final coolers to a pond located in a gravel and sand formation some 300 feet from the river bank. The pond has no direct outlet and the waste water may reach the river adjacent to the plant only by percolation through the soil.

Description of Phenol Recovery Process

The phenol recovery and treatment works at Hamilton is the first of its type operated on a full plant scale. An experimental installation was operated by the Koppers Company for a short time at Seaboard, N. J., using about 10 per cent of the volume of partially distilled ammonia liquor from a 3000-ton coke plant using the direct process of ammonia recovery.

The process consists essentially in passing inert gas saturated with steam in closed cycle round and round through the hot, partially distilled ammonia liquor. At one point in the gas cycle there is placed a scrubbing section containing hot caustic soda solution. The phenol passes from the ammonia liquor into the steam and gas mixture by virtue of its vapor pressure and in the caustic section is converted into sodium phenolate, which by reason of its much lower vapor pressure, remains in the caustic solution. Since the ammonia liquor and the caustic solution are both held at or immediately below their boiling points and since the tower and piping are covered with insulating material, there are virtually no heat losses.

At Hamilton the physical equipment consists of a steel tower 7 feet in diameter and 95 feet in height, a small blower, four small liquor pumps, two storage tanks, and the necessary piping. The operation temperatures are automatically controlled.

Operation of Recovery Works

In operating the recovery works the partially distilled ammonia liquor is taken from the bottom of the free still before it enters the lime leg. The dephenolized liquor returns by gravity to a point immediately below the point of take-off.

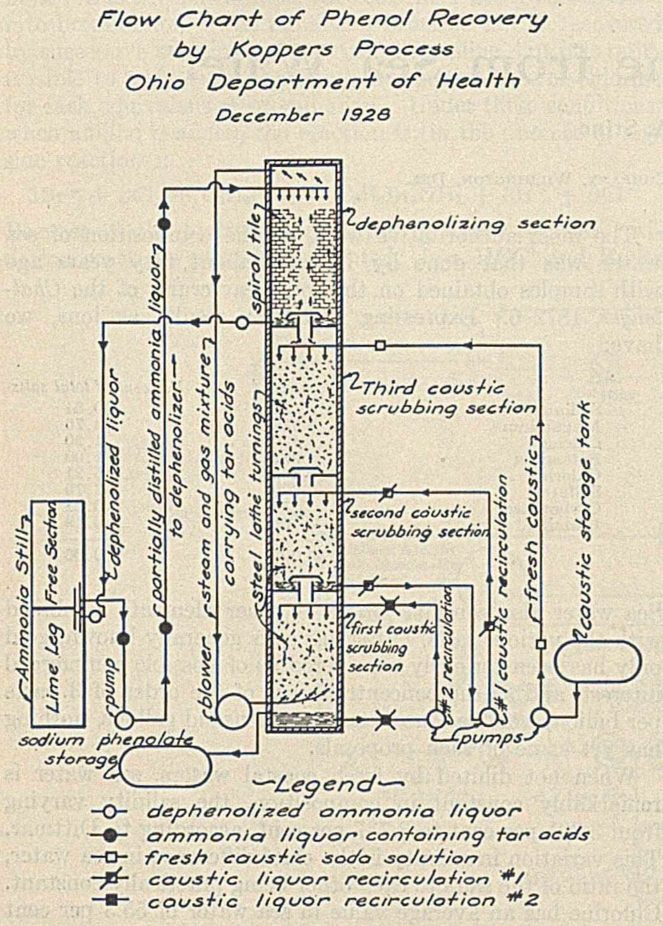
The partially distilled ammonia liquor containing phenol and other tar acids is pumped to the top of the upper section of the steel tower and introduced by means of sprays. This tower section is filled with spiral vitrified tile in order to break up the flow into small droplets and disperse it evenly over the entire area. Against the flow of partially distilled ammonia liquor in countercurrent manner is blown a mixture of about 90 per cent steam and 10 per cent air or other inert gas. As previously stated, the temperatures in the tower are held at or just below the boiling point. As the steam and gas mixture passes up through the top or dephenolizing section of the tower, the tar acids are vaporized and carried off. The steam and gas mixture is then drawn off from a point above the liquor sprays by the blower suction, passes through the blower, and is introduced into the lower part of the bottom section of the tower.

The tower at Hamilton has four sections, the top section being the dephenolizing section while the other three are for caustic-soda scrubbing. The three caustic-soda scrubbing sections are filled with steel lathe turnings to insure good distribution and intimate contact of the gas mixture and the soda solution as they pass through.

The fresh caustic-soda solution is introduced into the system at the top of the third caustic scrubbing section intermittently; enough being used to keep the steel turnings in the third section constantly wet. This caustic solution trickles down through the section and spills through an opening in the bottom into the top of the second caustic scrubbing section. It then passes down through this section, collecting in a well at the bottom. The caustic is drawn from this point by means of a pump and introduced back into the top of the same section through sprays. When the drainage from the third caustic scrubbing section raises the level of the well in the second to the overflow, a portion of the caustic solution drops into the top of the first caustic scrubbing section. Here again it trickles down through the packing and collects in a well. Another recirculating pump elevates the caustic liquor from this well to the top of the same or first caustic scrubbing section and introduces it through sprays.

The draw-off from the caustic scrubbing system is taken from the well at the bottom of the first caustic scrubbing section by means of an overflow to a sodium phenolate storage tank. The sodium phenolate is sprung with stack gas, and the phenol drawn off in salable form.

The steam and gas mixture containing phenol vapor, which is drawn from the top of the dephenolizing section by the blower suction, is introduced into the lower part of the bottom scrubbing section. The mixture then passes in a countercurrent manner through the first, second, and third scrubbing sections, successively, gradually losing its load of phenol vapor as it passes along. The steam and gas mixture freed of its phenol load, passes from the third caustic scrubbing section into the bottom of the dephenolizing section ready to receive more phenol vapor, and thus the process is continuously repeated. As stated previously, the dephenolized ammonia liquor returns by gravity from the bottom of the dephenolizing section to the lime leg of the ammonia still immediately below the point where the phenol contaminated liquor was originally removed. The liquor is then further distilled with lime to recover fixed ammonia.



Costs

Apparently the operation costs of this process are not burdensome. The phenol-contaminated liquor coming from the free still is at or just below the boiling point, and consequently the only heat loss is that required to raise the temperature of the fresh caustic solution introduced into the system to the tower temperature and radiation loss. Since the tower and piping are fully insulated, the radiation loss is low. Other costs of operation consist of power used in operating the motors which run the pumps and blower and a very small amount of labor. Under normal conditions the recovery works may be operated by the same men who have charge of the operation of ammonia stills. Caustic soda costs at this plant are largely charged off because of methods that have been developed for utilization of the soda in combination as sodium phenolate. Construction costs data for this works are not available. However, the cost of equipment, exclusive of overhead, should not be excessive. Under average conditions such a plant could be completed ready for operation in about 90 days.

Efficiency of Recovery Process

From the standpoint of efficiency the method is very promising. The phenol content of the weak ammonia liquor at Hamilton is between 2.5 and 3.0 grams per liter at the present time. With this process the phenol content of the dephenolized liquor has usually been below 100 p. p. m. and a 95 per cent removal or better is readily practicable. In some instances for an extended period the outlet concentrations have been considerably below those mentioned above.

Final Disposal of Wastes

As previously stated, the ammonia still wastes together with the benzene plant wastes are ponded in a gravel pit adjacent to the plant. This ponding of the wastes is an additional factor of safety at this plant against the pollution of Miami River, the stream which would normally receive the treated wastes. This stream at Hamilton has a drainage area of approximately 3660 square miles.

The U. S. Geological Survey maintains a stream-gaging station on Miami River at Venice, Ohio, about 14 miles downstream from Hamilton. The drainage area at this point is 3780 square miles. The lowest minimum daily flow on record at this station occurred in November, 1923, when the flow was 315 second-feet. During the cold-weather months of December, January, and February the lowest daily flow occurred in December, 1923, when the flow was 427 second-feet. The lowest yearly mean flow occurred during the period from October 1, 1922, to September 30, 1923, when the average flow was 2480 second-feet. The lowest mean monthly flow during the cold-weather months mentioned above occurred in December, 1917, when the flow was 920 second-feet.

Assuming a total phenol-contaminated waste-water discharge from a coke plant of this type of 40,000 gallons per day with a phenol content of 100 p. p. m., the flow in second-feet required to provide a dilution of 75 million parts water to 1 part phenol is approximately 463.

Conclusion

From the foregoing it would appear that this process is universally applicable and may be used at any coke plant which is located on a stream or body of water of sufficient size to afford the necessary dilution for the small amount of phenol contained in the resultant waste. The efficiency of phenol removal is high, the operation of the works is simple, the ground space required is small, the costs of operation appear to be attractive; and since this process is essentially one of steam distillation, the phenol obtained should be of exceptional quality. Therefore, it would seem that with this type of apparatus advantage can be gained by constant striving for high operation efficiency, and consequently the process gives promise of being of especial merit in locations where the continuous and certain protection of adjacent public water supplies is a matter of necessity.

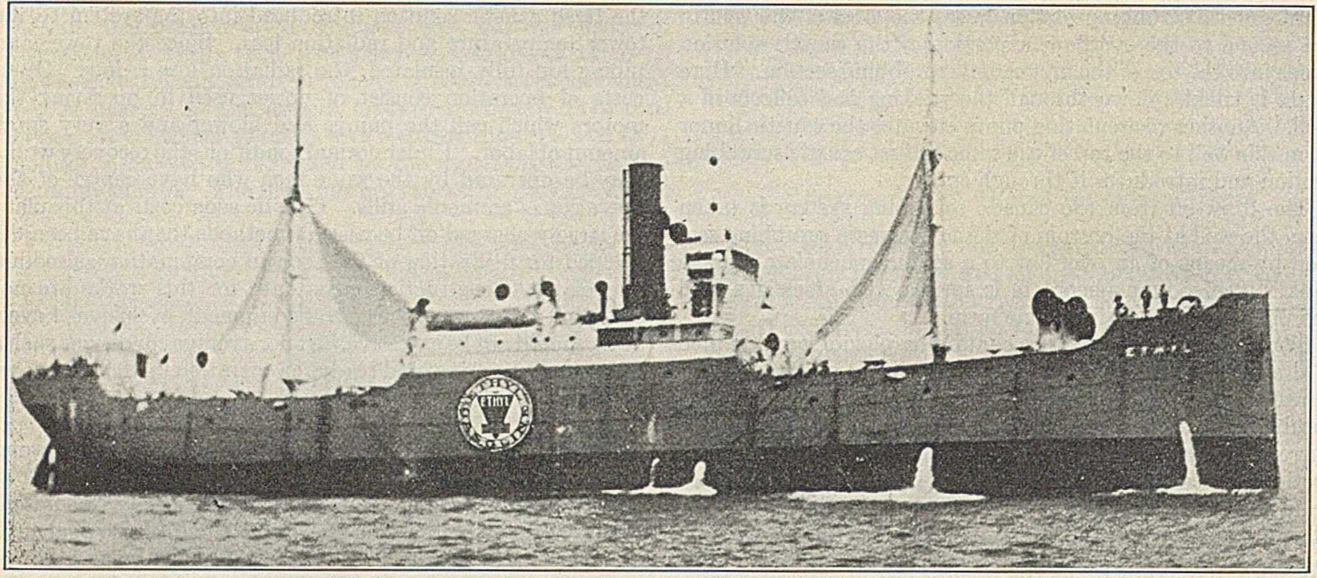


Figure 1—*S. S. Ethyl*

Recovery of Bromine from Sea Water[1]

Chas. M. A. Stine

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

THE chief, if not the sole, source of bromine in the United States has been the bromides recovered from salt brines. Up until a few years ago its supply was ample for the needs of industry. A new use for the element appeared, however, when it was incorporated with tetraethyl lead as a constituent of Ethyl fluid, which is blended with gasoline to form Ethyl gasoline. It shortly became apparent that the demand for bromine for this use might in time exhaust the then known sources, and the Ethyl Gasoline Corporation began to give consideration to new sources of the element which would be inexhaustible. In 1924 their laboratory, in coöperation with the General Motors Research Laboratory, devised a process for the recovery of bromine as tribromoaniline, which was successfully operated on a laboratory scale on brines as dilute as sea water, and which seemed to have possibilities for large-scale application.[2] Thereafter the du Pont Company and the Ethyl Gasoline Corporation undertook the development of this process for the recovery of bromine from the ocean. The results of this development will be described in the present paper, together with a brief discussion of the theoretical aspects of the problem.

Amount of Bromine in Sea Water

Bromine occurs in sea water to the extent of 60 to 70 parts per million (0.006 per cent), provided there is no coastal dilution with fresh water from the rivers. The area of the oceans of the globe is 139,295,000 square miles—compared with 57,250,000 square miles of land—with an average ocean depth of 3 miles. That this is truly an inexhaustible supply of the various chemicals contained in sea water, provided that suitable methods for their recovery could be devised, is evidenced by the fact that a plant producing 100,000 pounds of bromine per month would require 392 years to exhaust the bromine available in 1 cubic mile of sea water.

The most authoritative work on the composition of sea water was that done by Dittmar about fifty years ago with samples obtained on the four-year cruise of the *Challenger*, 1872–6. Expressing Dittmar's results as ions, we have:

	P. p. m.	*Per cent of total salts*
Sodium	10,722	30.64
Magnesium	1,316	3.76
Calcium	420	1.20
Potassium	382	1.09
Chlorine	19,324	55.21
Sulfates	2,696	7.70
Carbonates	74	0.21
Bromine	66	0.19
	35,000	100.00

Sea water also contains traces of other elements combined with the various salts, but so far as is generally known, gold only has been seriously considered as of possible commercial interest, and as the concentration is of the order of 3 parts per billion, worth about 1 cent per thousand gallons, nothing has yet come of such proposals.

When not diluted by fresh coastal waters, sea water is remarkably constant in composition, the salinity varying from 3.301 per cent to 3.737 per cent, according to Dittmar. This variation in salinity is the chief difference in sea water, the ratio of the salts to each other being practically constant. Chlorine has an average value in sea water of 55.3 per cent of the total salts, with a ratio of bromine to chlorine of 0.34 to 100. These figures correspond to a variation in bromine concentration in sea water of 62 to 70 p. p. m., depending on the total salinity of the sea water.

The salinity and bromine content of various samples of sea water obtained principally from the North Atlantic Ocean at various points along the east coast of the United States are given in tabular form herewith, according to our determinations. The effect of fresh-water dilution is especially noticeable in connection with those samples taken close to shore.

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[1] Received March 9, 1929.

[2] Edgar, U. S. Patent 1,662,305 (March 13, 1928); Andrew, U. S. Patent 1,662,355 (March 13, 1928).

SAMPLE	TOTAL SALTS	TOTAL HALIDES	RATIO HALIDES TO SALTS	BROMINE BY FACTOR 0.00188 × Total salts	0.00340 × Total halides
	Per cent	*Per cent*		*P. p. m.*	*P. p. m.*
Rehoboth, Del.	3.054	1.680	0.550	57	57
Ocean City, Md. (a jetty)	3.142	1.718	0.547	59	58
Ocean City, Md. (1 mile off shore)[a]	2.580	1.410	0.546	49	48
Miami, Fla.	3.636	2.004	0.551	68	68
Pablo Beach, Fla.	3.226	1.785	0.553	61	61
Jacksonville, Fla.	3.710	2.045	0.551	70	70
Houston, Texas	3.183	1.741	0.547	60	59
Beaufort, N. C. (1 mile off shore)	3.480	1.898	0.545	65	65
Beaufort, N. C. (near shore)	3.332	1.807	0.542	63	61
Beaufort, N. C. (well on beach)	2.743	1.497	0.546	52	51
Myrtle Beach, S. C. (1 mile off shore)	3.428	1.879	0.548	64	64

[a] Taken off the mouth of the inlet through which fresh water flows from the back bay.

Theoretical Considerations

Bromine exists in sea water in the form of its ion, the conversion of which into molecular bromine constitutes the first step required for its recovery by the tribromoaniline process. This is accomplished by means of chlorine, which effects a practically complete liberation of bromine. If aniline is added to such a mixture, however, only one-half of the bromine forms tribromoaniline, the remainder being reconverted into bromide ion. The remaining bromine can be recovered by successive additions of chlorine and aniline, but it is quite feasible to add at the beginning two equivalents of chlorine for each equivalent of bromine ion. Under these conditions, when aniline is added, the reaction is (in the absence of any side reactions):

$$3Br^- + 3Cl_2 + C_6H_5NH_2 = C_6H_2Br_3NH_2 + 3H^+ + 6Cl^-$$

Because of the hydrolysis resulting in dilute solution, oxidation reactions must be prevented, since HOCl and HOBr are very strong oxidizing agents. A chlorine solution in pure water in a concentration equal to that employed in the treatment of sea water is 99.99 per cent hydrolyzed; in other words, is essentially a hypochlorous acid solution. Since it is necessary to employ an excess of one equivalent of chlorine over the bromine present, in order to take care of the hydrobromic acid formed in the bromination of aniline, and since this excess chlorine partially hydrolyzes, there is some loss in yield. The formation of hypochlorous acid from the excess chlorine is controlled in part by virtue of the fact that both chloride and hydrogen ions depress the hydrolysis. With ordinary sea water the hydrolysis is reduced from 99.99 per cent to 72.75 per cent. We further reduced this hydrolysis by adding hydrogen ions in the form of sulfuric acid. Jakowkin[3] gives the following data covering the variation in the hydrolytic constant for chlorine with temperature:

$$\frac{H^+ + Cl^- + HClO}{Cl_2} = X$$

Temp., ° C.	0	15	25	39.1	53.6
$K \times 10^{-4}$	1.56	3.16	4.48	6.86	9.02

Calculations have shown that in the treatment of a sea water under standard conditions at 25° C. (77° F.) containing 200 parts sulfuric acid per million, the maximum proportion of the chlorine employed that could be hydrolyzed to hypochlorous acid was approximately 15 per cent of one equivalent based upon the bromine treated. Two equivalents of chlorine are actually added, one being required for the oxidation of the bromide ion resulting from the reaction of bromine and aniline.

Employing the above data and calculating the hydrolysis under various temperatures for the same acid concentrations, we have the following figures:

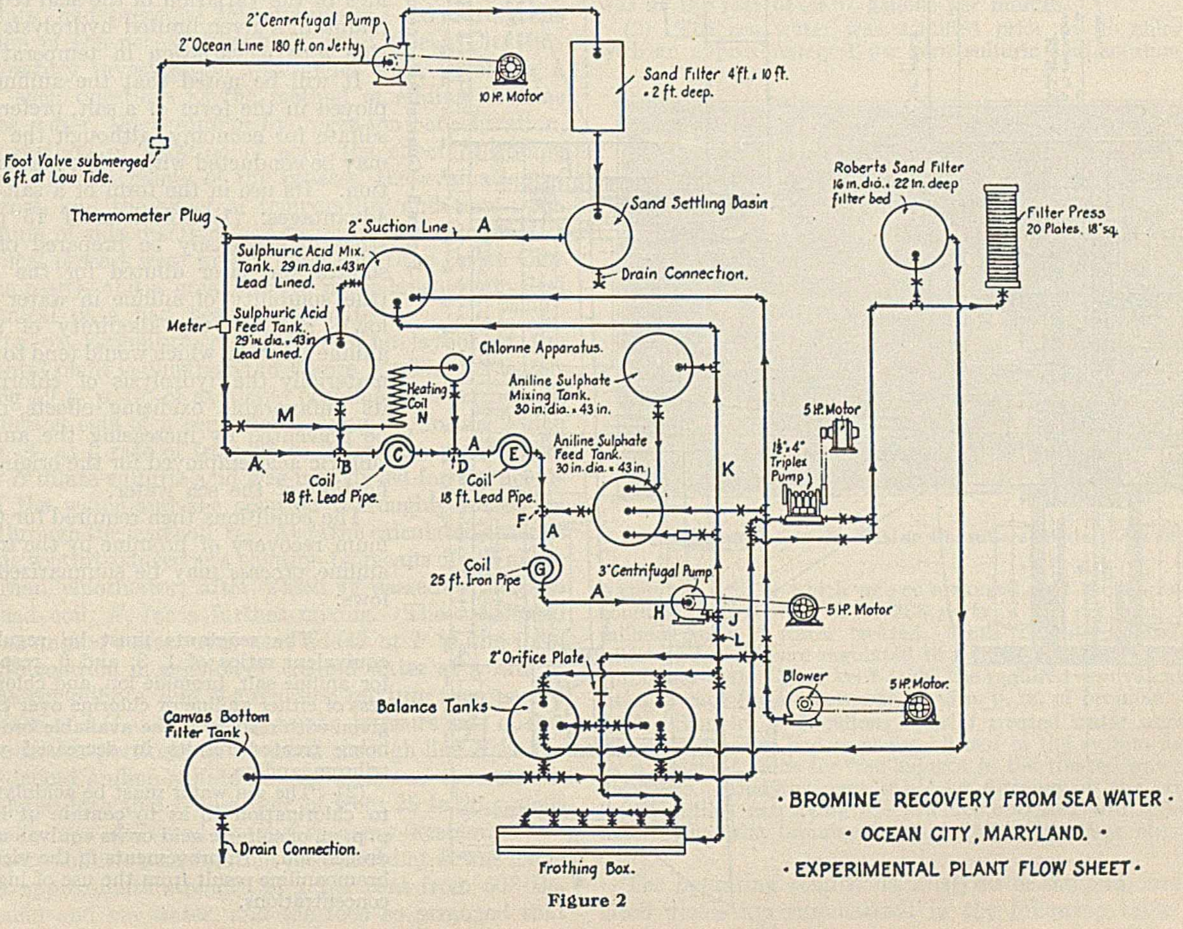

Figure 2

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[3] Jakowkin, *Z. physik. Chem.*, **29**, 613 (1899).

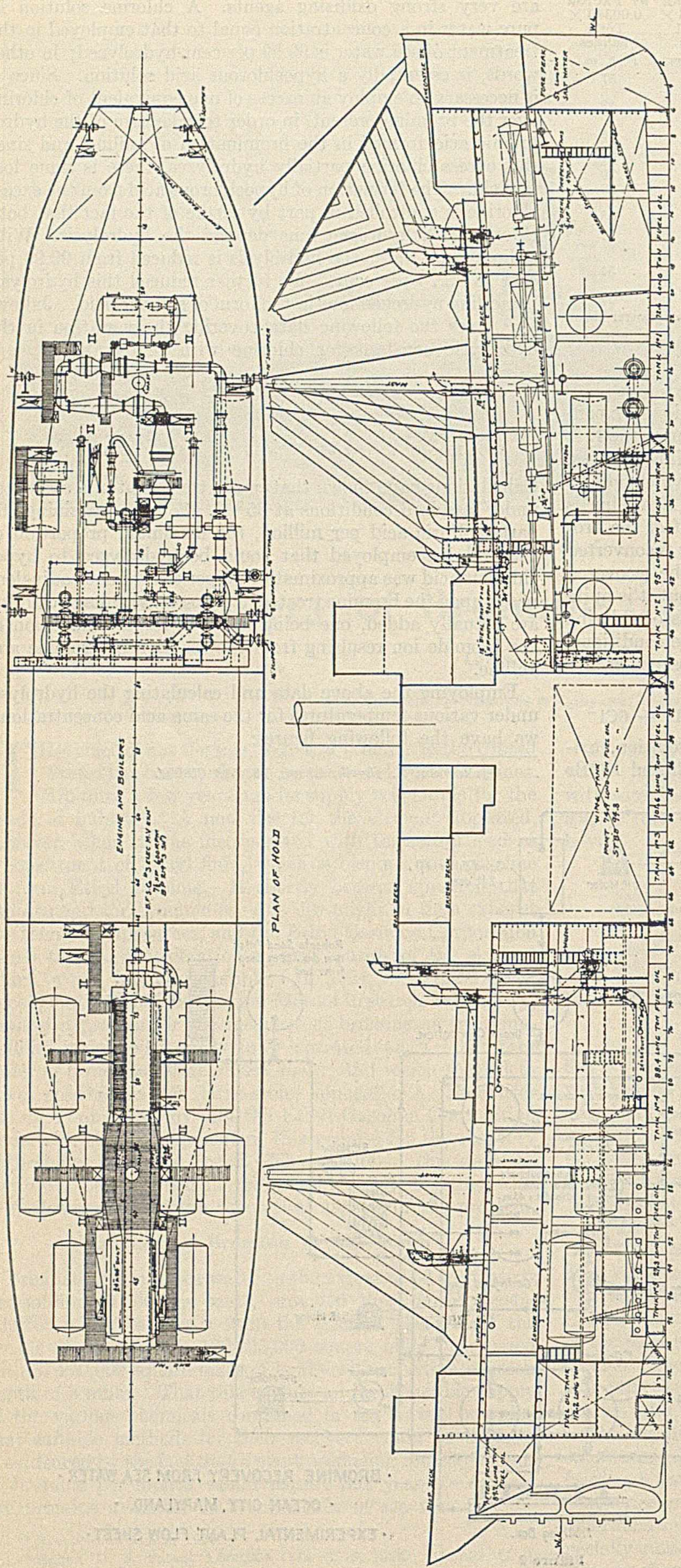


Figure 3—General Arrangement of Equipment on *S. S. Ethyl*

TEMPERATURE ° C.	K × 10⁻⁴	HYDROLYSIS Per cent
0.0	1.6	6.23
15.5	3.2	11.72
25.0	4.5	15.73
32.0	5.7	19.13

From these figures it can easily be seen that the temperature plays an important part, since oxidation of aniline by hypochlorous acid reduces the yield of tribromoaniline. Runs made at three temperatures on synthetic sea water in the laboratory actually yielded tribromoaniline as follows:

° C.	° F.	Per cent of theory
29.4	85	66 to 67
12.8	65	67 to 68
0	32	78 to 80

A 10 to 15 per cent increase in the yield is indicated by operating with sea water at 32° instead of 65° F.

On the other hand, it must not be forgotten that the percentage of chlorine hydrolyzed can be reduced by the use of larger amounts of acid, the limits being set only by a balance of the yield of product against the amount of acid employed. Thus the acid requirement to maintain a constant hydrolysis of 11.72 per cent at different temperatures may be calculated as follows:

TEMPERATURE ° C.	K × 10⁻⁴	H_2SO_4 REQUIRED P. p. m.
0.0	1.6	90
15.5	3.2	200
25.0	4.5	282
32.0	5.7	360

From these figures may be obtained some idea of the variation of the acid required to maintain a given limited hydrolysis of chlorine with a variation in temperature.

It will be noted that the aniline is employed in the form of a salt, preferably the sulfate for economy, although the reaction may be conducted with a dilute aniline solution. Its use in the form of a salt has two advantages: (1) Solutions of 15 per cent strength can easily be prepared of aniline sulfate and later diluted for the reaction (the solubility of aniline in water is quite low); and (2) the alkalinity of a dilute aniline solution, which would tend to increase materially the hydrolysis of chlorine with its unfavorable oxidizing effects, need not be prevented by increasing the amount of sulfuric acid employed for the original acidification of the sea water.

The conditions then required for the optimum recovery of bromine by the tribromoaniline process may be summarized as follows:

(1) The reactants must be regulated to equivalent ratios of 1, 3, and 6, respectively, for aniline salt, bromide ion, and chlorine; excess of either aniline or chlorine over the ratios given with respect to the available bromide ion being treated results in decreased yields of tribromoaniline.

(2) The sea water must be acidulated prior to chlorination so as to contain at least 200 p. p. m. of sulfuric acid or its equivalent in hydrogen ion. Improvements in the yield of tribromoaniline result from the use of higher acid concentrations.

(3) The reagents must be added separately in the order acid, chlorine, and aniline salt, and each brought to maximum dilution in its respective solution before combination.

(4) The mixing of the acidulated chlorine solution with the aniline salt solution must be as rapid as possible to bring all reactants to the proper equivalent ratios with respect to the bromide ion treated; otherwise losses of reactant materials occur through oxidation.

Semi-Works Development

In 1924, consideration was first given to the nature of the equipment necessary for the installation of a small experimental plant at Ocean City, Md., to determine the nature of the difficulties which might be encountered in attempting to recover bromine from sea water as tribromoaniline. A week or two of laboratory work, which had verified the earlier experiments, had preceded this discussion, and during the installation of the necessary equipment at Ocean City further laboratory investigation was under way, involving a study of such questions as the method of adding chlorine to the sea water, the optimum hydrogen-ion concentration, the best method of addition of acid, the effect of adding aniline at different points of the process, the evaluation of time factors, and the effect of temperature and time upon the amounts of side reactions. As a result the essentials of the chemical process were well in hand when the Ocean City plant was ready, and a great deal of miscellaneous physical and chemical data had been accumulated.

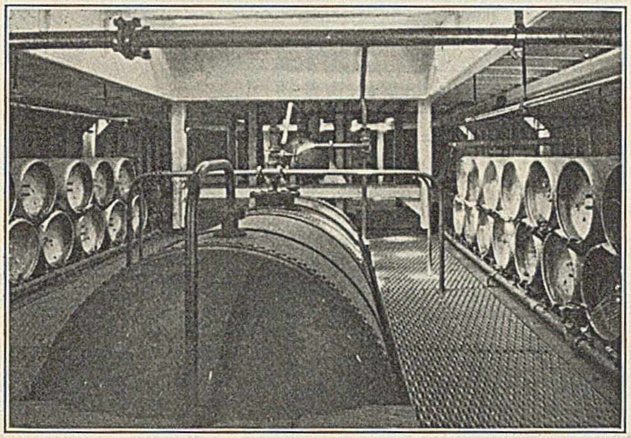


Figure 4—Heavy Chemicals Storage on *S. S. Ethyl*

Details of Experimental Plant—The layout of the experimental plant is illustrated in Figure 2. The sea water, containing 59 p. p. m. of available bromine, was introduced on the suction side of a centrifugal pump, *H*, into a 2-inch pipe line, *A*, at a rate of from 25 to 26 gallons per minute. At point *B* dilute sulfuric acid was introduced for the acidulation of the water and the solution thoroughly mixed by passage through the lead coil, *C*. At *D* the calculated amount of chlorine was introduced as a solution by means of a Wallace and Tiernan chlorinator, after which it passed through a second lead coil, *E*, for a further mixing. The calculated amount of aniline sulfate was next added at *F* in the form of a dilute solution in previously treated water at a rate of 10 gallons per minute, and the reaction mixture then passed through iron coil *G* and pump *H* to the pressure side of line *A*. Here at *J* a portion was returned through line *K* to the chlorinator and aniline sulfate mixing tank and the remainder, regulated by valve *L* to a flow of from 25 to 26 gallons per minute, was delivered to the recovery system.

The dilute sulfuric acid solution introduced at *B* was made up to an approximate strength of 1 per cent from 60° Bé. sulfuric acid and sea water, and the feed so arranged that its introduction could be made at various rates above and below the equivalence of 194 parts 100 per cent sulfuric acid per million of sea water treated. The chlorine was accurately measured within 2 per cent and introduced as a solution in treated water by means of a Wallace and Tiernan wet type of water chlorinator. The water required for the operation of this apparatus was taken from the return line *K* by way of the line *M* through a heating coil, *N*, where the temperature of the water was raised to 40° F. Preheating of the water was found to be necessary to prevent the formation of chlorine hydrate, a solid crystalline material that interferes seriously with the feed regulation in the chlorinator, since the water temperatures at Ocean City during the experimental operations varied from 38° to below 32° F. The operating pressure of the water feed on the chlorinator was approximately 26 pounds.

The aniline sulfate was introduced into the system as a 1.5 per cent solution in treated water and was measured accurately from the solution tank through a weir into the mixing tank, where it was further diluted with treated water before introduction into the reaction mixture at *F*.

The equipment and method of operation above described, while not ideal in all respects, represents the simplest and most economical continuous procedure that could be devised from the equipment available and within the limited time allotted for its experimental development and study.

Yields of Tribromoaniline—The yields of bromine obtained in the operation of this equipment were determined from samples taken during the course of three carefully controlled runs made under the following set of operating conditions:

(1) The sea water employed contained 59 p. p. m. of bromine, but was treated as containing only 55 p. p. m. to avoid difficulties arising from the variable delivery of the pump. The treatment was at the rate of 25.67 gallons per minute.

(2) The sea water was acidified prior to its chlorination with an approximately 1 per cent sulfuric acid solution in sea water, the feed of which was so arranged that the acid addition could be varied from 97 to 388 parts of 100 per cent acid per million parts of water treated. Both the chlorine and aniline sulfate solution were regulated to feed as accurately as possible (probably within 3 per cent each) the required equivalent quantities of each for a treatment of 55 p. p. m. of bromine.

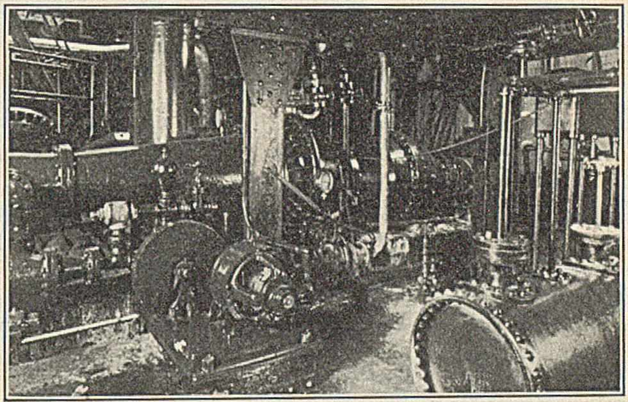


Figure 5—One of the Mixing Chambers on the *S. S. Ethyl*

(3) Samples of 5 gallons each of treated water were taken when equilibrium had been established in the system as shown by a constant value for free halogen in the treated water at the discharge. Analyses were made by filtering off the crude tribromoaniline, extracting the product obtained with ether, and determining the bromine in the total solids thus obtained.

The operating conditions, analyses of samples, and calculated yields are summarized in the following table:

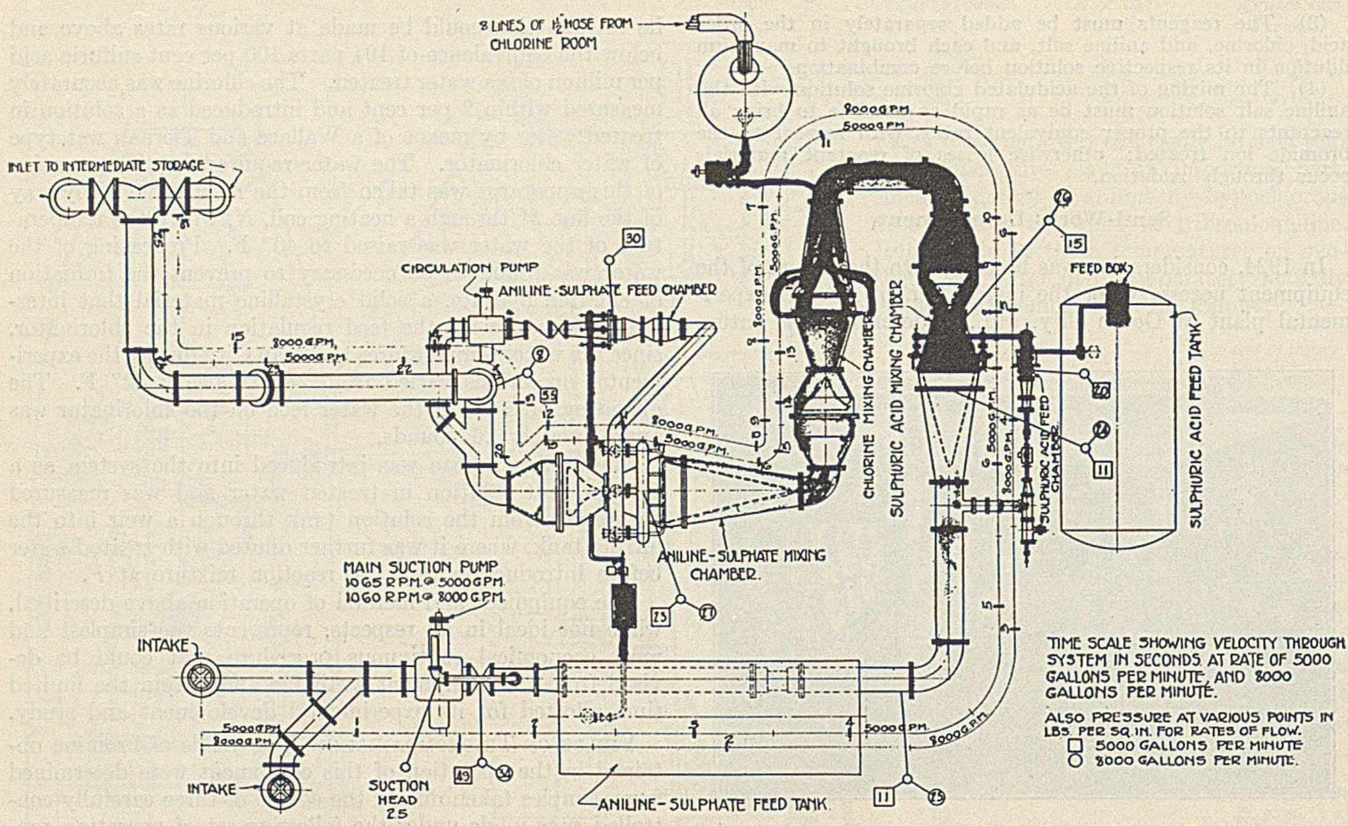


Figure 6—General Arrangement of Chemical Treating System with Various Points of Injection of Chemicals

	Run 1	Run 2	Run 3
OPERATING CONDITIONS			
Rate of water flow, gallons per minute	25.67	25.67	25.67
Bromine treated, pounds per hour	0.7012	0.7012	0.7012
66° Bé. sulfuric acid, pounds per hour	1.335	2.67	4.74
Sulfuric acid, p. p. m.	97	194	388
Chlorine, pounds per hour	0.6188	0.6188	0.6188
Aniline sulfate, pounds per hour	0.4211	0.4211	0.4211
Free halogen in discharge calculated upon chlorine charged, per cent	9.4	5.64	4.62
SAMPLE			
Weight, grams	16,300	16,600	15,600
Recovered ether-soluble, grams	0.6266	0.8435	0.6151
Bromine by analysis, per cent	56.93	53.71	58.07
CALCULATED YIELDS			
Yield in per cent bromine treated	41.33	51.54	43.24
Bromine recovered, pounds per hour	0.2898	0.3614	0.3032
Tribromoaniline made, pounds per hour	0.3987	0.4972	0.4171

The yields obtained of 41.33 and 51.54 per cent, respectively, for acid ratios of 97 and 194 parts per million of sea water treated, show, as would be expected, an increasing yield with an increase of acid. The lower yield obtained in run 3 is not in line and no explanation can be satisfactorily offered for the low value obtained unless it is assumed that an error was made in the recovery or analysis of the sample.

The percentages of free halogen found in the discharge further emphasize the necessity for accurate control of reagents and the provision for adequate means of mixing, since it may be seen from the table that increasing the acid ratio did not completely eliminate a considerable proportion of unused halogen.

The yields in percentage of bromine treated, while not equal to the best performances obtained in laboratory batch treatments (70 per cent), demonstrate the possibilities of a continuous pipe-line process and illustrate a few of the factors, the control of which is necessary to the successful operation of a continuous process, in which the maximum dilution of reagents is less and the time of reaction shorter than for a batch operation. The filter cake obtained from the various experimental runs at Ocean City was very high in foreign matter, a typical analysis showing: 47.6 per cent tribromoaniline, 45.1 per cent ash, and 7.3 per cent organic material. The ash proved to contain, among other things, 64 per cent silica (sand) and 18 per cent iron oxide. It is believed that difficulties in filtration that developed later were caused to a large extent by the gummy nature of the combination of very fine sand, always in suspension along the seashore, and the organic material discharged into the ocean by the rivers and their connecting tributaries.

Methods of Analysis for Bromine—The analysis of bromine on all samples of water examined was made by an indirect volumetric method in which the total halides were determined by the Volhard silver nitrate titration and a factor was taken as representative of the bromine content. This method was devised by Dittmar, who, in the examination of representative samples of sea water, found that there was a variation of only 0.1 per cent between the true bromine content as found by direct analysis and by applying his factor to the total halides.

In operating a continuous process for the recovery of bromine, the variation in the volume of water handled by the pumps is estimated at from 2 to 5 per cent. The feed of reagents is probably limited to an accuracy of from 1 to 2 per cent, so that there is an unavoidable average variation of close to 3 per cent for which allowance must be made in the treatment of the water. This difficulty is practically solved by undertreating the water sufficiently to insure that the treatment is never made in excess of the actual bromine content. Under these conditions any slight error arising from an indirect determination of the bromine content of the water by the use of Dittmar's factor becomes negligible.

Conclusions from Small-Scale Operation—Altogether the experimental work at Ocean City demonstrated that bromine could be recovered from sea water, but it also indicated clearly that the success of the process depended upon substantially complete dispersion of accurately controlled amounts of the necessary chemicals, and upon as rapid as possible dispersion. It also indicated that serious difficulties would arise from operating on water containing any appre-

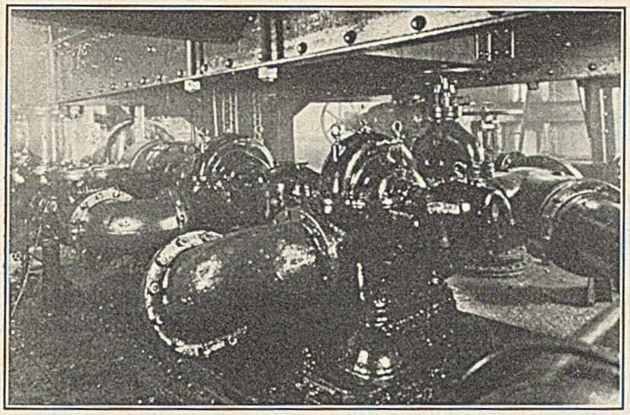


Figure 7—Some of the Pumps on the *S. S. Ethyl*

ciable amount of suspended matter. It was largely the last problem, coupled with the advantages of flexibility in scene of operation, that suggested that the next stage of development should be placed upon a ship.

Large-Scale Development

The S. S. Ethyl—A number of steamships were inspected and a lake-type cargo steamer, *The Lake Harminia*, a steel boat 253 feet 8 inches long, 43 feet 8 inches beam, 4200 tons dead weight, was purchased (Figure 1). This boat was delivered to the Bethlehem Shipbuilding Corporation's plant in Wilmington on February 12, and her conversion into a floating chemical plant was begun. On April 18 her overhauling and the installation of the chemical equipment had been completed and the ship was on her way down the Delaware River for a preliminary mechanical test, which was carried out April 18, 19, and 20. The test proved in every way satisfactory, and the ship was returned to the Harlan plant for the completion of a number of minor details left unfinished pending the tryout of the major equipment. A week later the ship proceeded to the du Pont Company's Dye Works wharf to take on chemical supplies, and a day or so later put to sea. Process runs were accomplished on May 2 and 3.

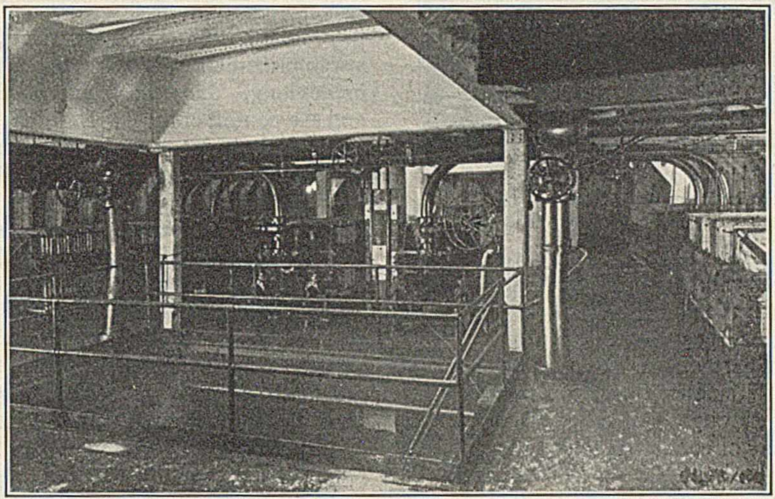


Figure 8—Filter-Press Deck on the *S. S. Ethyl*

Equipment—*Capacity*. The capacity of the equipment was based upon an estimate of a recovery of 100,000 pounds of tribromoaniline. If it is assumed that the water contains 70 p. p. m. of bromine, that a yield of 70 per cent may be obtained, and that the ship would operate 25 working days per month, it is a simple matter to calculate that 7000 gallons of sea water per minute must be treated. This volume of water practically excluded every type of equipment but a pipe line and also excluded such filtration systems as would involve settling basins, etc. It was necessary to develop special equipment for extremely rapid mixing on a large scale and an accurate and simple control of the chemicals required for the process. Details of this equipment will be discussed below.

General Plan. Figure 3 shows the general arrangement of the equipment in the ship, and Figure 4, a photograph taken in the after storage hold of the boat, shows how this hold was utilized for the storage of the various chemicals required in the process. Storage capacity for approximately 500,000 pounds of 66° Bé. (93.19 per cent H_2SO_4) sulfuric acid and 50,000 pounds of aniline were provided in steel tanks placed underneath the "'tween decks." The liquid chlorine storage installation was planned to consist of 1-ton drums, having a total capacity of 66 tons of liquid chlorine. This was calculated on the basis of a month's supply.

Considerations of safety made it imperative to construct all acid and storage tanks without bottom outlets. The piping arrangement was such that both acid and aniline could be moved from storage to points of consumption by means of compressed air. In view of the stresses and strains to which the storage tanks would be subjected when the ship was at sea, these tanks were placed in deep saddles to which welded lugs, attached to the tank, were securely bolted. In addition, large strap bands were laced around the tanks and suitably and securely attached to the tanks' supporting members.

Mixing Devices. An important feature of the process was the type of mixing device developed for practically instantaneous mixing of the sea water with the various chemicals required. The injection and turbulence chamber shown in Figure 5 illustrates this device. The basis for this design was the assumption that relatively large injection rings must be provided to spread out the water flowing through the system and that subsequently it must be forced through turbulence chambers in order that the mixing might be sufficiently effective. The turbulence chamber illustrated in Figure 5 represents in principle the device used throughout the mixing system for: (1) the dilution of the 66° Bé. acid to approximately 1 per cent and the disper-

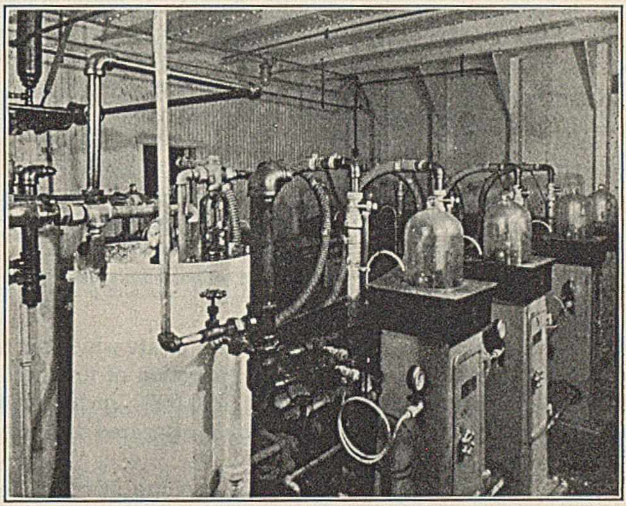


Figure 9—Chlorine Control Room on the *S. S. Ethyl*

sion of this weak acid throughout the mass of the water being processed; (2) the injection and dispersion of the chlorinated water as supplied to it by the Wallace and Tiernan chlorinators; and (3) the injection and dispersion of aniline sulfate.

The general arrangement of the chemical treating system with the various points of injection of the chemicals is shown diagrammatically in Figure 6. In this connection it is interesting to note that the total time elapsing during the passage of the water at a rate of 5000 gallons per minute (rate actually used on ship's trial trip) from the point at which all the chemicals had been added to the filter process was approximately 5 minutes. An important part of the installation consisted of the arrangement for recirculating approximately 40 per cent of the treated water through the annular ring mixing chamber, so that at the time of contact between the acidified and chlorinated sea water and the sea water containing the aniline sulfate, aniline sulfate may have as great a dispersion in the circulating and mixing system as possible. It has previously been pointed out that the bromine content of sea water is 70 p. p. m. Theoretically, then, for each 3 atoms of bromine, 6 atoms of chlorine and 1 molecule of aniline should be simultaneously presented at the point of combination. Since the atomic weight of bromine is 79.916, 7000 gallons of sea water must contain approximately 1.576 pounds of aniline uniformly distributed throughout this volume of sea water. This is a high dilution to attempt to produce as nearly instantaneously as possible.

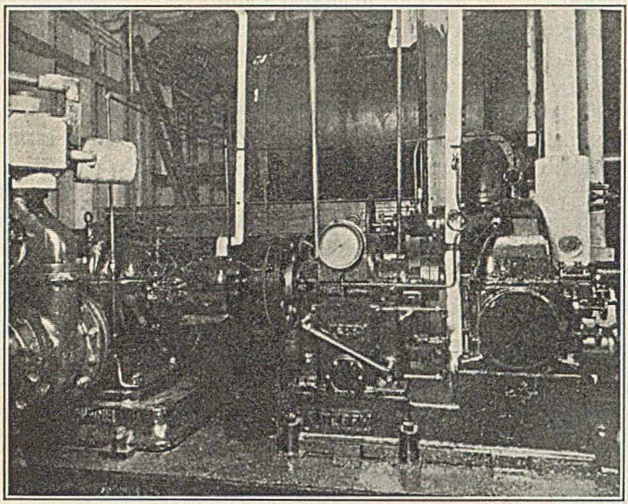


Figure 10—Equipment in Place on the *S. S. Ethyl*

RESULTS OF TEST RUNS—A log sheet of one of the trial runs is as follows:

Run 1—May 2, 1925

Rate of water flow	4750 gallons per minute
Bromine content	67.7 p. p. m. by weight
Acid treatment	223 to 500 p. p. m. by weight
Chlorine	3477 pounds per 24 hours

Aniline sulfate—regulated approximately to best appearing conditions of treated water—i. e., to the formation of maximum cloud of precipitate.

Treated water contained a fine white precipitate which microscopic examination revealed to be a collection of fine needle crystals—average diameter 0.0001 to 0.0002 inch, length 0.0008 to 0.0010 inch. These crystals appeared in collections of small flocks or groups.

Treated water filtered through 4500 square feet of filtering surface under pressure of 30 pounds per square inch gage to yield a clear slightly pink filtrate.

Duration of run	3 hours
Weight of wet product, filter cake	1616.5 pounds
Moisture in cake	69.5 per cent
Weight of crude dry product	493.0 pounds
Bromine content	59.26 per cent
Tribromoaniline content	81.52 per cent
Ash—ferric oxide	2.83 per cent
Undetermined matter	15.65 per cent
Theoretical yield from treatment at rate of 2377 pounds of chlorine per 24 hours	489.9 pounds bromine
Actual recovery	292.2 pounds bromine
Yield	59.64 per cent

DESCRIPTION OF PROCESS USED ON SHIPBOARD—The essential ingredients for the treatment of sea water for the recovery of bromine in the form of tribromoaniline are: 66° Bé. sulfuric acid, liquid chlorine, and aniline sulfate.

The 66° Bé. acid is held in bulk tank storage in the after hold, the daily requirements being blown by air to process storage tank in forward hold. From this tank it is fed through a constant-head float-controlled feed box to the suction line of a positive-pressure Blackmer type pump, which delivers it to the sulfuric acid dilution mixer, the discharge of which, of approximately 1 per cent acid, goes to the main sulfuric acid mixing and turbulence chamber, when it is dispersed uniformly in 3 seconds (at the rate of 8000 gallons per minute flow) to a dilution approximately 200 p. p. m. Liquid chlorine is stored in 1-ton containers which are approximately 2 feet 6 inches in diameter and 6 feet 8 inches long. Liquid chlorine weighs 90 pounds per cubic foot and the containers at 68° F. will be at a pressure of 100 pounds per square inch. Provision has been made to store sixty-six 1-ton containers (gross weight 3300 pounds) between decks in the forward part of the after hold. The liquid chlorine is fed from two or more containers through a header and feed line to Wallace and Tiernan type M. S. V. chlorinators, eight in number, located between decks in the after end of the forward hold. Immediately preceding the chlorinators are evaporators, steam-heated, to insure the delivery of chlorine to the chlorinators being in the form of gas. The chlorinators are vacuum-operated by means of a water jet forming part of the water to be chlorinated.

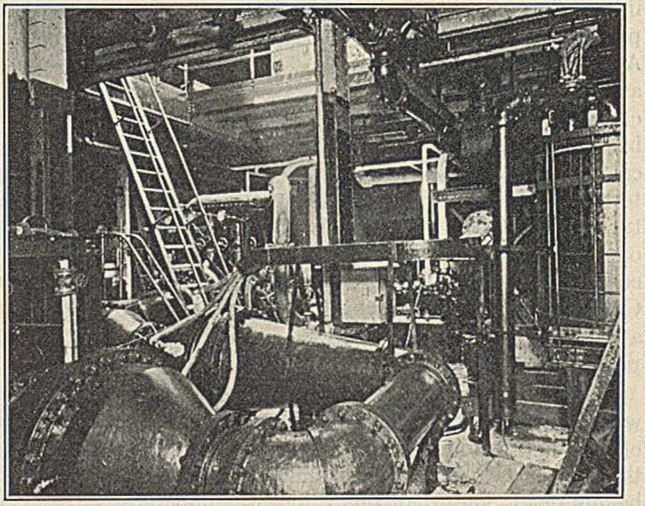
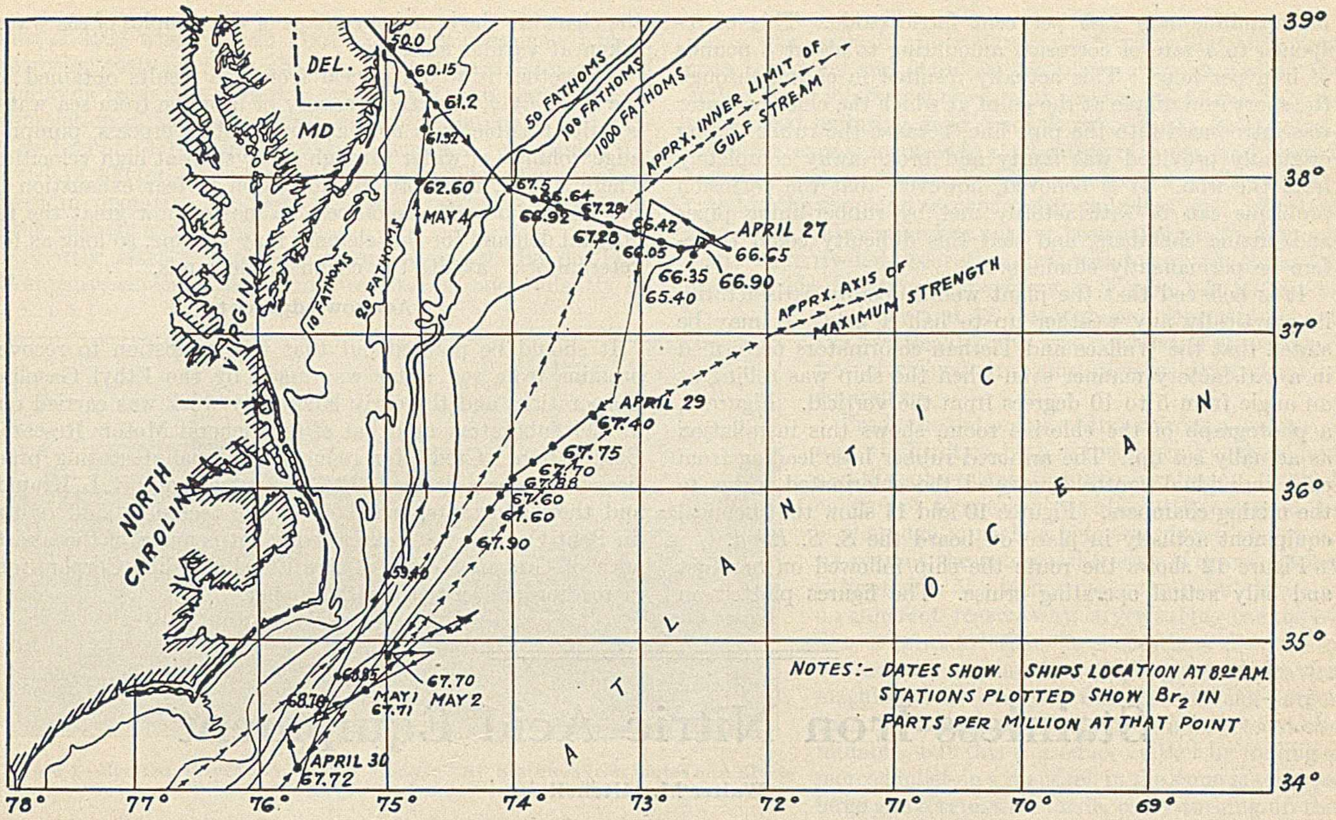


Figure 11—Equipment in Place on *S. S. Ethyl*

Water leaving the chlorinators contains dissolved chlorine gas determined by the rate of feed for which the machines may be calibrated on the basis of pounds per day. Six of the machines installed were of the constant-feed type rated at 750 pounds per 24 hours, while the other two can be controlled to feed from 750 to 300 pounds and from 360 pounds to zero, respectively. With this arrangement any desired rate of chlorine feed could be obtained. The chlorinated



NOTES:- DATES SHOW SHIPS LOCATION AT 8^{00} A.M. STATIONS PLOTTED SHOW Br_2 IN PARTS PER MILLION AT THAT POINT

Figure 12—Route Followed by the *S. S. Ethyl* on First and Only Actual Ocean Voyage for Recovery of Bromine

water discharged from the chlorinators is delivered through rubber-lined armored hose to a rubber-lined chlorinated water feed tank to the bottom of which is connected an Olivite (rubber-lined) pump, which in turn delivers, by means of an eight-lead manifold, the thoroughly mixed chlorinated water (about 0.5 per cent of chlorine) to the chlorine mixing and turbulence chamber. Complete dispersion of the chlorine to a dilution of about 64 p. p. m. is obtained in 3 seconds.

Aniline (for the manufacture of aniline sulfate) is stored in steel tanks in the after hold, the storage capacity being approximately 50,000 pounds. It is delivered by air to a small measuring tank in the forward hold, from which it goes to the lead-lined aniline sulfate mixing tank underneath, at which point the proper amount of sulfuric acid and sea water is added to give the desired strength to the aniline sulfate formed by the reaction. Normally it is planned to produce aniline sulfate of about 15 per cent strength. After the reaction is completed (which operation is performed daily), the aniline sulfate is blown across the ship to the aniline sulfate storage tank. From this tank it is fed through a constant-level float-controlled feed box to the aniline sulfate feed pump, which delivers it to the aniline sulfate dilution mixer, which in turn injects through thirty-six nozzles the diluted aniline sulfate into the aniline sulfate mixing and turbulence chamber, and thence to the storage tanks. The dilution is brought about by recirculating about 2600 gallons per minute of the processed sea water through the aniline sulfate dilution chamber.

The mixing of the dilute aniline sulfate with the acidified and chlorinated sea water results in the formation of tribromoaniline crystals which are about 0.001 inch long and one-fifth of this in diameter. The reaction is practically instantaneous in that samples taken 1 second after going through the mixing chamber showed the reaction to be completed. The total time through the various mixing chambers, for a rate of 8000 gallons per minute is about 10 seconds, during which the three different chemicals must be consecutively added and completely dispersed before the complicated reaction resulting in tribromoaniline takes place. From the storage tanks the processed water is delivered by steam-turbine-operated compound centrifugal pumps to ten recessed-type, wood-plate Schriver filter presses of fifty plates each, located between decks in the forward hold. These presses were dressed with XX chain filter duck and also ordinary weave, with the indications that either grade of filter cloth would be effective. The filtrate was at all times clear with the operating pressure of 30 to 35 pounds per square inch remaining constant throughout the run. It is believed that a press could be operated on an 8-hour cycle, during which time approximately 70 pounds of filter cake would be produced, which would contain from 65 to 70 per cent moisture. The dry cake would in turn be approximately 80 per cent tribromoaniline.

Allowing 1 hour for cleaning and getting back into service, a filtering rate of 1000 gallons seems conservative, so that if the ship were operated at a rate of 8000 gallons per minute, as proposed, eight presses in service would permit of one being down for repairs and one being cleaned.

COSTS—The cost of essential materials, based on a yield of 70 per cent and a bromine content of the sea water of 68 p. p. m., would be $0.1770 per pound of bromine. The total of the other charges is problematical, since the ship was operated only a short time.

General Comments

A number of minor difficulties were encountered in connection with the operation of the bromine ship, such as fluctuating rate of sulfuric acid feed, due primarily to the orifice-regulating valve at the outlet on the float control feed-box being made of hard rubber, which decomposed under the action of the acid. There was some corrosion at various points. It will be recalled that the ash content of the tribromoaniline was 2.83 per cent ferric oxide. This corresponds to a rate of corrosion amounting to about 3 pounds of iron per hour. This actually resulted in eating through the short iron nipple at the point at which the chlorine water was introduced into the pipe line, because the rubber lining originally provided was faulty and broke away completely from the iron. It is believed, however, that the corrosion problems can be satisfactorily met by rubber-lining pipes and mixing chambers, and that this difficulty could therefore be permanently eliminated.

It is believed that the plant would operate satisfactorily in practically any weather up to half a gale. It may be stated that the Wallace and Tiernan chlorinators performed in a satisfactory manner even when the ship was rolling at an angle from 5 to 10 degrees from the vertical. Figure 9, a photograph of the chlorine room, shows this installation as actually set up. The armored rubber hose leading from each individual control conveyed the chlorinated water to the mixing chambers. Figures 10 and 11 show the chemical equipment actually in place on board the *S. S. Ethyl.*

Figure 12 shows the route the ship followed on her first and only actual operating cruise. The figures plotted on the chart are the bromine content of the samples of sea water taken at various stations.

Altogether it would appear from the results obtained on the *S. S. Ethyl* that the recovery of bromine from sea water is quite feasible by a continuous pipe-line process, pumping huge volumes of water through the system at high velocities. There should, therefore, be no reason to fear exhaustion of the world's bromine resources, no matter how great the industrial demand for this element may become, so long as the "eternal sea" awaits the chemist's demands.

Acknowledgment

It should be pointed out that the suggestion to recover bromine from sea water was made by the Ethyl Gasoline Corporation, and the early laboratory work was carried out in their laboratory and that of the General Motors Research Corporation. Credit for reduction to manufacturing practice of the process is due to E. R. Armstrong and R. L. Kramer and their assistants, members of the technical staff of the du Pont Company. Acknowledgment is made of the assistance of Graham Edgar, of the Ethyl Gasoline Corporation, in reading and criticizing this paper.

Stainless-Iron Nitric Acid Equipment[1]

Walter M. Mitchell

Central Alloy Steel Corporation, Massillon, Ohio

That ammonia may be converted into nitric acid by an oxidation process has been known as a theoretical possibility for many years,[2] but it is only within the last few years that the process has been developed to the point of commercial production. The success of this development should not be considered as due solely to the skill and ingenuity of the chemist. It is due as well to the availability of suitable materials which, satisfactorily resisting the corrosive action of the acid and capable of fabrication into the required forms, have made possible the construction of the necessary plants and equipment. These materials[3] are the iron-chromium alloys containing 16 to 20 per cent chromium and known, because of their low carbon content, as stainless irons.

Nature and Properties of Stainless Iron

Stainless steels, alloys of iron and chromium containing 11 to 13 per cent chromium with sufficient carbon (0.30 to 0.40 per cent) to confer hardening properties, have been known in the form of cutlery for some fifteen years, but owing to their intrinsic hardness cannot be produced in forms suitable for the construction of chemical plant equipment. The desire for a more workable material—one that could be produced in such forms as sheets, tubing, wire, etc.—led to the development of the stainless irons. Since the corrosion resistance of the stainless alloys depends upon the ratio of chromium to carbon content, and since carbon was not desirable on account of the hardening effect produced by it, stainless irons have been produced by lowering carbon and increasing chromium content.

Experiments and tests with stainless iron showed remarkable resistance to oxidation and in particular to nitric acid. The first stainless iron produced may be considered an offspring of the original stainless steel and was made with virtually the same chromium content (12 to 14 per cent) but with materially lower carbon (0.12 per cent maximum). This alloy is resistant to a great degree to all concentrations of nitric acid, but not sufficiently so to the more dilute acids. To obtain the necessary resistance to the more dilute acids, it has been found necessary to increase the chromium content (16 to 20 per cent), and specifications for stainless iron for nitric acid equipment virtually all demand a minimum of 16 per cent chromium. Higher chromium (above 20 per cent), while increasing corrosion resistance to a slight degree, does not improve mechanical properties of the alloy, so that fabricating difficulties may be increased. To lessen the hardening tendency carbon should be maintained low, under 0.10 per cent. Other elements, with the exception of nickel or silicon, are present in stainless iron largely as impurities and should be maintained as low as is consistent with good melting practice.

A word of caution at this point is advisable. While the 12 to 14 per cent chromium stainless irons cost less than those of higher chromium content, a reasonable margin of safety as regards corrosion resistance is a most desirable precaution. Resistance to nitric acid increases with chromium content, and the insurance of longer plant life by the use of a higher chromium alloy will more than compensate for the questionable advantage of a slight saving in the initial cost of the installation.

The stainless irons are suitable only for the construction of plant equipment for acid that is produced from ammonia. The acid prepared from Chile saltpeter has too high a content of chlorides, iodides, etc., and unless these impurities are removed stainless iron will be attacked.

Development of Use in Nitric Acid Industry

The first experiments with stainless irons in connection with their application to the nitric acid industry began in the sum-

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[1] Received March 2, 1929.

[2] Taylor, Ind. Eng. Chem., **19**, 1250 (1927).

[3] Mitchell, *Trans. Am. Soc. Steel Treating*, February, 1929.

mer of 1923 when the du Pont Company commenced plant corrosion tests on these alloys. About a year later a small ammonia oxidation unit was constructed, and the successful completion of this experiment led to the designing and construction of a large plant at Gibbstown, N. J., containing upwards of 200 tons of stainless equipment. This plant has now been in operation for over two years and has apparently been entirely successful.

Shortly after experiments were begun by the du Pont Company, similar experiments were made independently by the Atmospheric Nitrogen Corporation, a subsidiary of the Allied Chemical and Dye organization. The satisfactory results of their experiments resulted in the construction of a large unit at Hopewell, Va., in which upwards of 500 tons of stainless equipment were used. Since that time additional plants have been erected by the du Pont Company, the General Chemical Company, the Newport Company, the Grasselli Chemical Company, the Hercules Powder Company, the Atlas Powder Company, and others. The total stainless iron now in service in nitric acid equipment is between 4000 and 5000 tons, and represents a value of upwards of $5,000,000.

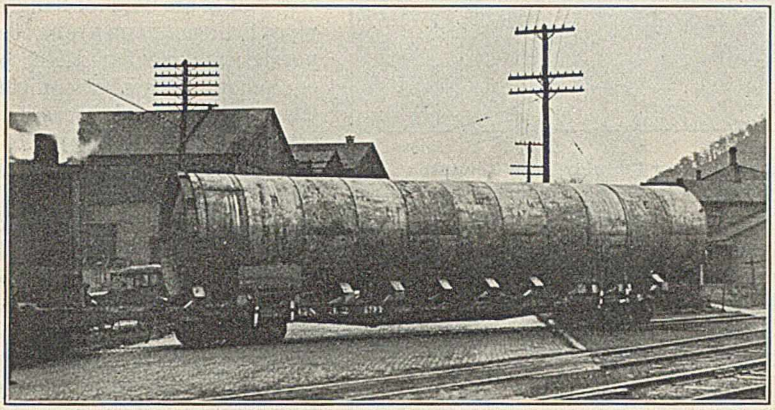

Figure 1—Riveted Absorption Tower. Enduro "A" Stainless Iron Plates and Rivets Fabricated by Struthers-Wells Co., Warren, Pa.

Methods of Fabrication

Equipment for an ammonia oxidation plant includes absorption towers, heat exchangers, converters, pipe lines, valves, etc., etc. The first question encountered in the consideration of stainless irons for plant construction was the fabrication of the equipment. Could large-size plates be rolled, single-piece flanged and dished heads of large diameter be formed, was seamless drawn tubing available, etc.? And, if these articles were procurable, could they be welded or riveted together in permanent fashion? Fortunately, the production of large plates and single-piece dished heads presented no unexpected difficulties. The procurement of these articles is now limited only by the range of the equipment available for their production and by the willingness of the steel mills to coöperate with the expectant customer.

The usual methods of fabrication are welding and riveting. When fabrication of stainless equipment was first considered, welding was at once ruled out because of the very unsatisfactory state of the art at that time. The production of rivets that would stay put also presented difficulties, because of the propensity of the straight iron-chromium alloys to become brittle if overheated. Workmen accustomed to driving ordinary steel rivets heated the stainless rivets to the usual temperatures (1900° to 2100° F.) only to find that when cold the heads snapped off spontaneously or at the slightest blow of the hammer. Many experiments were necessary before the proper processing of the rivet stock and the rivets themselves was learned. Fortunately, such difficulties have now been overcome and stainless-iron plates may be riveted together with joints, which careful tests show to be fully as strong and enduring as if made from ordinary boiler steel. However, care is required in the heating of rivets, and riveted structures have been confined to such size as could be fabricated in the shop and transported to the plant site. For this reason field fabrication has not yet been attempted. Figures 1 and 2 are riveted absorption towers and show what may be done in this direction. The tower in Figure 1 is 10 feet in diameter and 52 feet high, and represents about the practical limit in size, because of the difficulties of railway transportation of larger pieces of equipment.

Production of seamless drawn tubing presented many difficulties, both in the piercing of the billets and the subsequent drawing operations. Careful control of temperature is absolutely essential, as is thorough annealing between successive draws. At present the external diameter of drawn tubing is limited to $5^1/_2$ inches maximum; but there is no inherent reason why larger tubing cannot be drawn provided there is a sufficient demand to warrant the outlay for the larger and heavier machinery necessary. Seamless tubing larger than $5^1/_2$ inches outside diameter is at present obtainable, but this is produced either by forging a pierced billet on a mandrel, in the same manner as large gun forgings are made, or by turning up the outside of a large cylindrical billet and removing the core by a trephining operation—in either case a laborious and costly procedure.

Large-size pipe for conduits is successfully made by riveted construction, as shown in Figures 3 and 4. While this requires skill and careful work on the part of the fabricator, it is an entirely feasible proposition. Such pipe can be caulked so as to be both gas- and water-tight.

Generally speaking, stainless iron of the proper analysis for nitric acid plant construction can be fabricated into any form or shape which can be made from ordinary boiler steel, provided due regard be given to the individual peculiarities of the metal. In handling this metal it must be remembered that it is both harder and tougher than steel. Forming and bending operations should therefore be conducted more slowly than with plain steel; furthermore, excessive temperatures must be strictly avoided. Figures 5 and 6, showing a heat

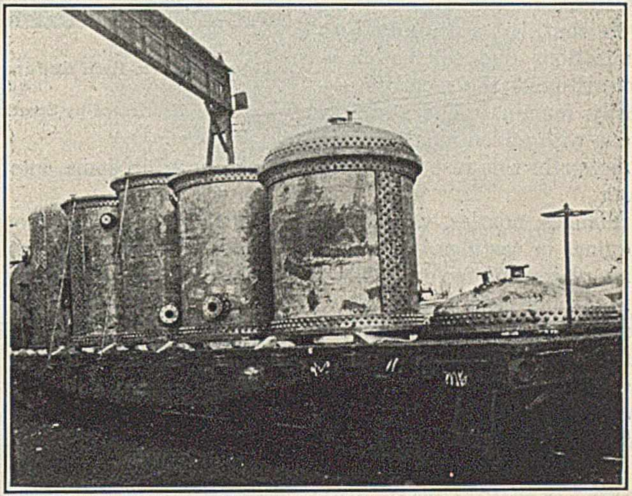

Figure 2—Stainless Iron Bubbler Tower
Fabricated by Downingtown Iron Works, Downingtown, Pa.

exchanger and a tray plate, illustrate what can be done with proper handling.

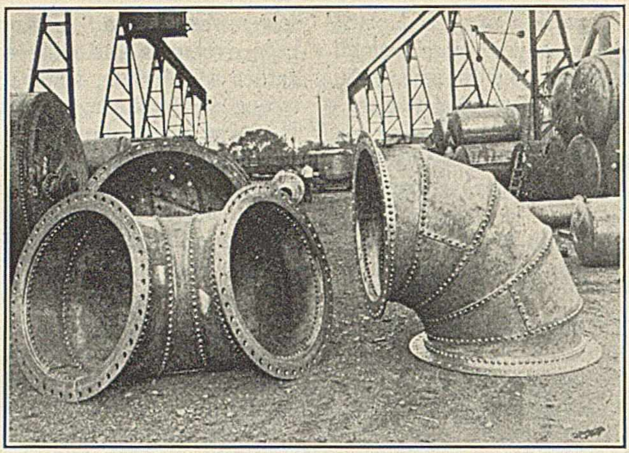

Figure 3—Large-Diameter Stainless Iron Conduit
Fabricated by Downingtown Iron Works, Downingtown, Pa.

There has been much discussion on the relative merits of welding and riveting as a method of fabrication. The majority of the chemical manufacturers, the larger companies in particular, absolutely bar welded construction for any of the larger equipment unless it is physically impossible to produce the desired piece of equipment in any other way. The high temperatures of welding produce a crystalline structure essentially different from that in the adjacent metal. In addition, there is always opportunity for inclusions of slag, particles of oxide, etc. In the straight chromium alloys it is practically impossible to produce a homogeneous structure in the weld and the adjacent metal by any process of heat treatment. Therefore, there may be, and generally is, localized corrosive attack, either in the weld itself or in the metal closely adjacent to it. In addition to the probability of local attack, there is to be considered the brittleness, or lack of ductility, due to the coarse crystalline structure formed during welding, which is characteristic of straight iron-chromium alloys, and which, as already stated, can be removed to a limited extent only by heat treatment. Naturally, there has been a great improvement in welding technic since the stainless irons were first introduced, but limitations due to the characteristics of the metal necessarily remain. The stainless irons with added nickel are far superior in this respect, and will be discussed in some detail later.

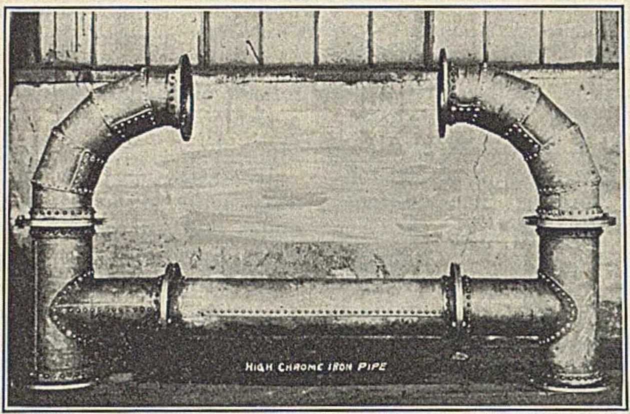

Figure 4—Ten-Inch Enduro "A" Stainless Iron Conduit Pipe and Fittings
Fabricated by Struthers-Wells Co., Warren, Pa.

Flanges, nozzles, valves, and pipe fittings are made from forgings or castings. Castings are made with higher carbon than plates, tubing, etc. The low-carbon analysis, when cast, will usually have blowholes, porosities, etc., and to overcome this, carbon must be raised to 0.30 to 0.40 per cent. With this high carbon, resistance to nitric acid, provided the chromium is maintained high, is apparently not affected. Casting technic has improved greatly in the last four years and reasonably good castings may now be procured from a number of foundries which specialize in stainless metals.

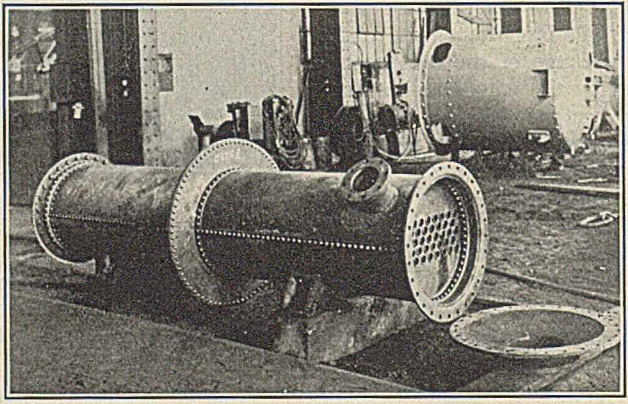

Figure 5—Enduro "A" Stainless Iron Air Heater
Fabricated by Struthers-Wells Co., Warren, Pa

Welding, plugging, or caulking of defective castings is usually prohibited. This has caused almost endless controversy between the foundries, who desire to salvage as many castings as possible, and the chemical manufacturers, who do not desire material which may eventually prove defective. Much can be said on both sides and the decision will depend largely upon the nature of the defect.

Forgings are used for flanges, pipe fittings, pump shafts, nozzles, and similar pieces of equipment where a better metal than that obtainable in castings is required. Forgings present no particular difficulty in manufacture other than that introduced by the greater stiffness of the metal as compared with ordinary carbon steel. Forgings may be made from billets or bar stock of the same analysis as plates and tubing and, if properly made, are free from such defects as blowholes or porosities. If high pressures are to be withstood, forgings have a great advantage over castings in their freedom from such defects. However, owing to the considerable machine work required, pipe fittings, such as ells, tees, etc., made from forgings will be high in price compared to castings.

Stainless-Iron Tank Cars

For bulk shipment of acid, stainless-iron tank cars have been under consideration for some time, but their high cost has prevented actual construction until very recently. A number of these are now on order and the first stainless-iron tank car was put in service by the du Pont Company about eight months ago. Fabrication of tank cars presents no difficulties above those incurred in the construction of stationary tanks. The container tank only is made from stainless iron. The framework and trucks are of the customary steel construction. Naturally, because of the shocks and vibrations to which the tank car is subjected, great care must be observed in the inspection of the materials, and the general design must be sufficiently heavy to insure sufficient strength and stability.

Alloys Containing Nickel

All of the equipment, so far described, has generally been made from the straight iron-chromium alloys. But for certain purposes, where welding is unavoidable, the stainless irons with added nickel have a notable advantage. Alloys of this kind will usually run 18 to 20 per cent chromium, 7 to 10 per cent nickel, and carbon under about 0.16 per cent. They were introduced by Strauss, of the Friedrich Krupp Company, in Germany about fifteen years ago, but until recently have attracted little or no attention in this country. Their advantages are now beginning to be appreciated and they are rapidly supplanting the straight iron-chromium stainless irons. The addition of nickel results in a number of advantages: first, increased corrosion resistance; second, prevention of coarse crystalline growth at elevated temperatures; third, it produces what is metallurgically known as an "austenitic" alloy. Such alloys, of which manganese steel is a well-known example, are characterized by great toughness and ductility, entire freedom from any tendency to hardening on sudden cooling, and the property of being non-magnetic.

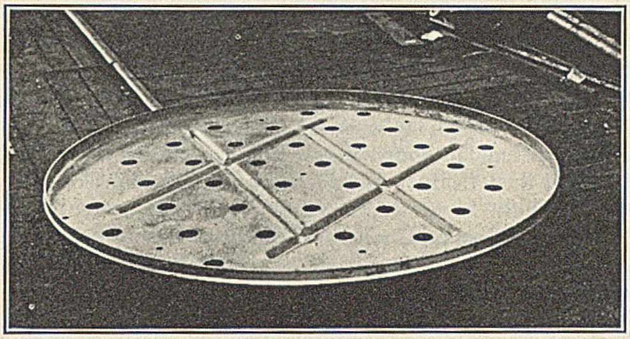

Figure 6—Stainless Iron Tray Plate
Fabricated by Struthers-Wells Co., Warren, Pa.

These alloys possess higher resistance to both hot and cold nitric acid than the straight iron-chromium alloys. As they are practically free from the grain growth associated with high temperatures, welds remain tough and ductile, and fabrication by welding is a reasonably safe procedure as far as maintenance of physical properties is concerned. The question of preferential corrosion resistance, however, remains; but it is possible to heat-treat these alloys so that structural differences between the weld and the adjacent metal may be greatly broken down, thus materially lessening the tendency to localized attack. Patents covering the heat treatment of this alloy were granted to Strauss, as well as patents covering the analysis.

Shipping drums for nitric acid have been somewhat of a problem since their suggestion some five years ago. The glass carboy, long a standard shipping container for acids, is far from ideal. Hence, stainless irons were welcomed by chemical industries as the potential means of solving the transportation phase of the nitric acid problem. The straight iron-chromium alloys were originally used for construction of experimental drums, but owing to the brittleness of the welds, by which the drums were of necessity fabricated, it was found practically impossible to meet tests imposed by the Bureau of Explosives and the Interstate Commerce Commission, notwithstanding that various types of construction were used.

Because of the greater ductility and toughness of welds made from the chromium-nickel stainless alloys, later experiments have been made with drums constructed from them and these drums have passed successfully all varieties of mechanical tests that could be devised. In use, however, the first lot experimentally made showed the effects of unrelieved strains in the metal after some six or seven months in service. This is thought to be the result of insufficient annealing after welding. Other drums, which have had a more complete annealing treatment, are now in service. It is believed that these will be satisfactory, although the time in service is too short for confirmation of this. They are constructed of various sizes, usually 15-, 30-, and 55-gallon capacity, and provided with cast or forged flanges and bungs. The Hackney, or two-piece construction (Figure 7), with equatorial weld, has proved the best type in all mechanical tests.

Outlook

Looking toward the future, any prediction of what may be expected is extremely hazardous. When we consider the advances made in metallurgy of corrosion-resisting alloys during the last five years, any assertion of what can or what cannot be done is manifestly unwarranted. The two years' successful operation of the first du Pont plant indicates that stainless irons have attained an established position in nitric acid manufacture. However, the greater advantages of the chromium-nickel stainless irons over those containing chromium as the only alloying agent indicate that they will be carefully considered in the future, and may replace the latter altogether. It is rather doubtful if new alloys will be produced with qualities widely different from those at present known. The combinations of chromium, nickel, iron, silicon, etc., which produce workable alloys are fairly well known. Numerous experiments have determined the limits of the useful composition ranges with considerable certainty. There is a possibility that small additions of some other metal, such as molybdenum which is known to increase resistance to mineral acids, will prove desirable. But until the present equipment has been subjected to longer tests in service, we do not know that such additions are even necessary.

Figure 7—30-Gallon Enduro KA2 (Chromium-Nickel Stainless Iron) Shipping Drum
Fabricated by Pressed Steel Tank Co., Milwaukee, Wis.

If any improvements are to be expected, these lie in the direction of improved quality of metal, which may be looked for with increased demand and resulting increased tonnage production. Increased tonnage will result in mills and equipment devoted exclusively to the production of these alloys, and under such advantageous conditions improvement in quality should inevitably follow.

Thermal Expansion of Tantalum—The Bureau of Standards will shortly publish the results of an important investigation on the expansion of pure tantalum for various temperature ranges between −310° and +930° F. Tantalum expands more than tungsten or molybdenum, but less than iron.

It is highly resistant to chemical corrosion and is finding use for dental instruments, surgical tools, pen points, filament wire for incandescent lamps or thermionic tubes, cathodes for use in electrochemical analysis, and electrolytic valves for the manufacture of rectifiers.

Present Trends in Dust Recovery

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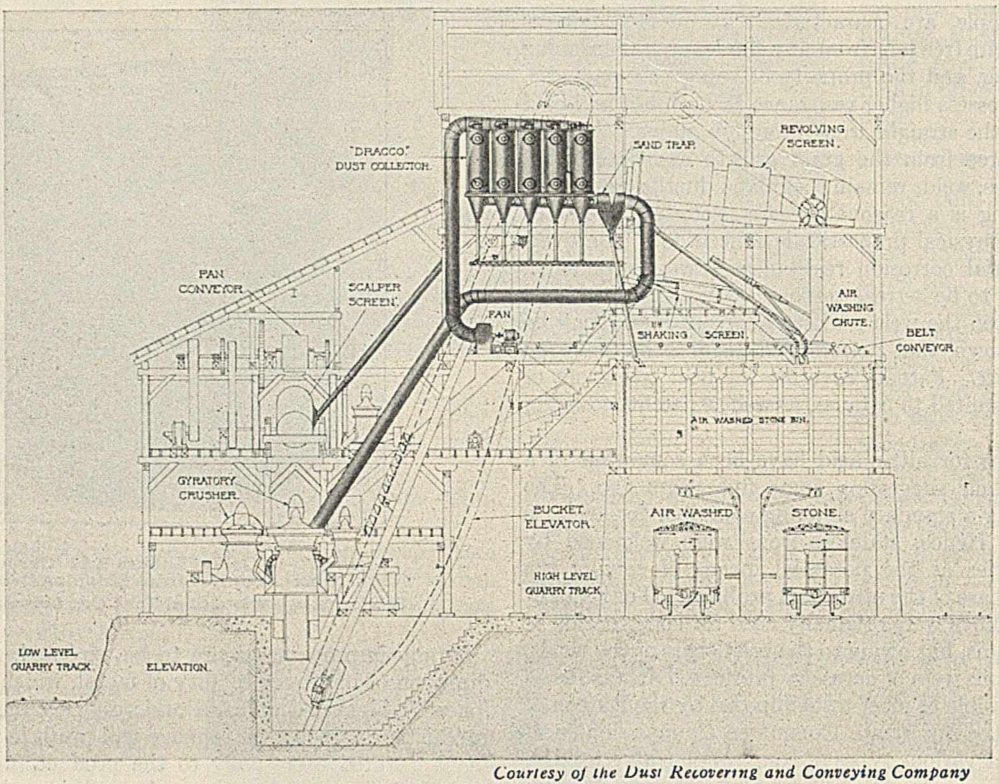
Dust resulting from industrial operations has been regarded from three successive viewpoints. It was first considered somewhat in the light of an unavoidable nuisance. Dust-producing plants, such as cement mills, located themselves as far as possible where there were no neighbors to complain of the objectionable conditions which they produced. They then went into operation with calm resignation to the inevitable high rate of labor turnover, the gradual destruction of equipment, and the loss of material resulting from this policy. When the plant happened to be a flour mill and a stray spark started things going, the company either went out of business or built a second plant as dusty as the first.

This attitude, reminiscent of the way our ancestors of the Middle Ages regarded disease, gave way gradually as it came to be realized that it represented neither good engineering nor good business. It was natural that the viewpoint toward industrial dust should then grow to be that of prevention only. Equipment was developed to reduce or to eliminate the production of free dust, and to collect the dust from operations in which its production seemed inevitable. This attitude regarded dust as a nuisance, in some cases as a positive danger, but as essentially nothing more than a waste material.

Recently, however, engineers with investigative minds and imagination have been discovering that there is no such thing as a waste material. In the field of dust elimination they have found frequently that the finely divided material taken out of circulation was either a valuable fraction of the main plant output or a by-product worth more per unit of weight than the main product. They have also been discovering that dust-collecting apparatus may form a very efficient unit process in the preparation of such materials as dried milk and fruit juices, gas black and bone black, pulverized coal, and dyes. As a result of this development new stimulus has been given to the design and application of ingenious systems to still other fields.



Courtesy of the Dust Recovering and Conveying Company

Figure 1—Elevation of Crusher Plant Making Road Gravel

Air filters recover dust from gyratory crushers, scalping screens, and chutes to storage bins. This dust is sold as agricultural limestone. Enough was recovered during the first year of operation to pay for the filter installation, while the dust-free gravel produced commanded a special bonus.

Types of Equipment for Dust Collection

The various types of apparatus for the removal of dust from gas streams may be conveniently classified for discussion on the basis of what can be done with the dust after it is collected. Certain systems, intended chiefly for the removal of ordinary incidental dust from the atmosphere, do not allow of ready recovery of the separated material. It is obvious that these systems might be applicable to some cases where a dust resulting from a manufacturing process had negligible value but must be removed in order to prevent a nuisance. Some of them are also used for the recovery of precious metal dust, but for general use economic considerations necessitate the types of apparatus allowing simple recovery.

Care must be exercised in analyzing any particular problem of dust collection from the viewpoint of the value of the material collected, since it is entirely possible that an apparently worthless dust may have some profitable means of utilization. One firm engaged in producing crushed limestone for road gravel installed a dust removal and collection apparatus in order to obtain a bonus for dust-free gravel. It subsequently developed that the fine dust collected had sufficient value as agricultural limestone to pay for the equipment within a year.

Systems for Dust Collection without Recovery—Only brief mention will be made of those types of equipment which are intended chiefly for the removal of incidental dust from air, and which leave the separated material in a condition from which it cannot readily be recovered. Two general

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[1] Associate editor, Industrial and Engineering Chemistry.

types exist. The first type depends upon a water spray, arranged in any one of a number of ingenious ways, through which dust-laden air is passed, with removal of those particles that are wetted by the spray. The second type, loosely styled a "filter," depends upon passing the air to be cleaned through small, tortuous channels, the surfaces of which are covered with some sticky medium which holds all particles impinging upon it. Use is found for equipment of these two types chiefly in cleaning the cooling air supplied to motors and generators, and in purifying the air circulated in public buildings or used in such special processes as the drying of gelatin, in which contamination by atmospheric dust and air-borne bacteria must be minimized.

Systems for Dust Collection with Recovery—All types of equipment for dust collection other than the two mentioned above allow the ready recovery of the fine material separated out. Such recovery is, of course, not always practiced, not even when it might be profitable. It is possible, however, and where recovery becomes an important factor in the choice of equipment the following types find application.

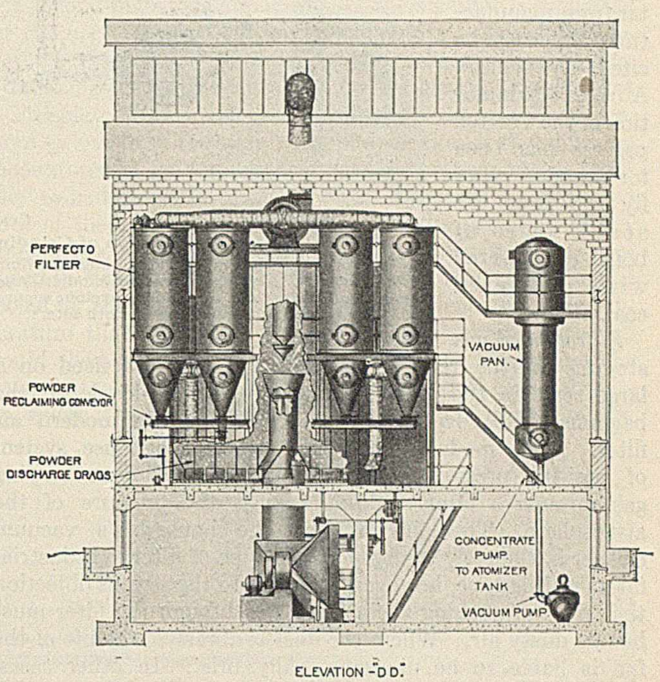
Equipment for the recovery of dust from gas streams may be classified on the basis of the principle utilized. The four following types result: (1) sedimentation by gravity; (2) separation by centrifugal force; (3) electrical precipitation; (4) filtration.

Sedimentation by gravity is the oldest and simplest principle used for the removal of dust from gas streams. The settling chamber has been a familiar nuisance in the smelting industry for years. It is now practically obsolete as an agency for dust removal, though it still serves as a cooling flue for hot gases. Fair separation of large particles can be obtained in the settling chamber under carefully controlled conditions of rate of flow, turbulence, and temperature of the gas stream. The inadequacy of the method is evident, however, when it is realized that a spherical particle of unit density and a diameter of 1×10^{-2} cm. settles at a rate of only 30 cm. per second in absolutely still air. Such a particle represents merely the largest range of industrial dusts. Although a settling chamber will serve for the practical removal of such particles, the space requirement for the sedimentation of fine dusts is prohibitive and the separation is unsatisfactory.

Centrifugal force is utilized for dust collection in the cyclone separator, which exists in many varieties, all of which have the common characteristic of passing a dust-laden stream of gas in a spiral path at a velocity sufficient to cause the suspended particles to be thrown out against the containing wall, down which they drop by gravity into a container at the bottom. Cyclones are generally constructed as a cylindrical housing ending in a conical bottom, with a tangential inlet to the upper part of the cylindrical section and an outlet for cleaned gas through an internal axial duct leading out through the top. The various dimensions of cyclones are adapted to give gas velocities suitable for the separation of various materials, or of various sizes of these materials. Velocities as high as 1500 feet per second are claimed for some special cyclones of small diameter.

Although cyclone separators operate most efficiently upon gases containing particles of uniform large size, it is possible to use two of them in series for the simultaneous removal and partial sizing of dust having a considerable range of particle diameter. As in the case of the settling chamber, however, fine dusts cannot be efficiently recovered in a cyclone separator.

One advantage of the cyclone is its simple and rugged construction without moving parts. It can be fabricated from special alloys to handle streams of corrosive gases, and it can handle hot gases. It is, in fact, frequently found good practice to use a cyclone for cooling a hot gas stream and simultaneously removing the coarser particles from it, as a preliminary to complete dust removal in a filter, which can only be used at low temperatures.



Courtesy of the Dust Recovering and Conveying Company

Figure 2—Elevation of Small Dried-Milk Plant

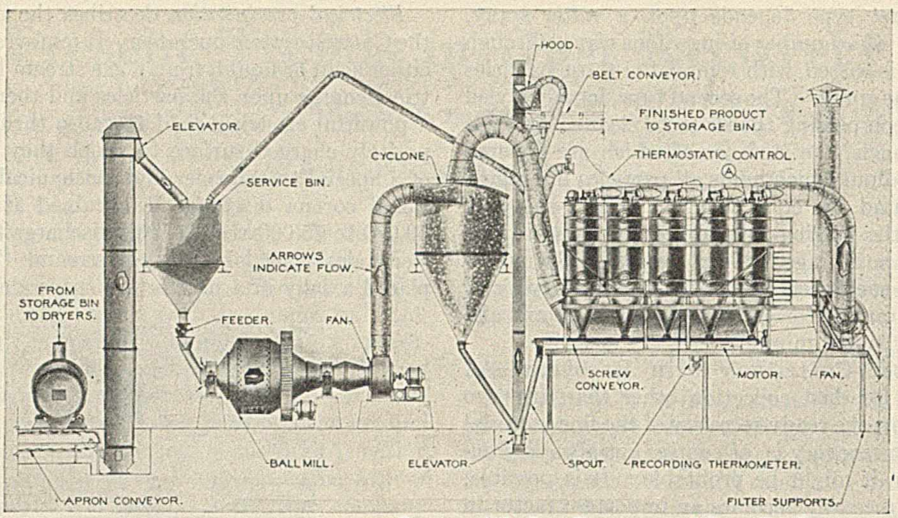
Air filters recover completely the valuable material carried out of the spray drier by the effluent air stream.

Electrical precipitation describes the principle upon which the Cottrell system operates. It removes suspended particles, either solid or liquid, from a gas stream by producing an electrical charge upon the particles and then utilizing the pull of a powerful electrical field to cause them to travel to an oppositely charged surface to which they adhere. By the use of a special transformer and mechanical rectifier, a unidirectional corona discharge is obtained at a potential of from 50,000 to 75,000 volts. This discharge takes place from wire electrodes placed in the gas stream. These electrodes are placed axially in a pipe or are suspended between plate surfaces, the pipe or plates being connected to the opposite side of the high-potential line. The suspended particles in the gas stream passing through the corona discharge are charged by adsorption of ions from the ionized gas and then move toward the oppositely charged surfaces upon which they deposit, being removed either by gravity or by mechanical cleaners.

The efficiency of removal of suspended particles is a function of the length of exposure of the gas stream to the electrical field within the precipitator, but is practically independent, within ordinary limits, of the concentration of the suspended material. The efficiency guaranteed for ordinary installations is 90 per cent, although units may be built to give practically complete recovery if it is desired. The power consumption varies from 5 to 10 kilowatt-hours per million cubic feet of gas treated.

The Cottrell apparatus has two fields of operation in which it is unrivaled. The process of electrical precipitation is not affected by temperature; hence it may be designed for operations up to 650° C. or 1200° F., and its construction is so simple that it may be readily made from corrosion-resistant materials and employed for the treatment of acid gases, particularly acid mists. Electrical precipitation is therefore the general solution for the removal of suspended particles from a gas stream which is corrosive or must be treated while hot. Since cyclone separators also can operate under these conditions, they are sometimes used as preliminary separators in series with Cottrell units.

Of the processes in which electrical precipitation finds application, the recovery of oxides and of acid mists from smelting operations, of potash dust from cement kiln gases, and the removal of tar from manufactured gas may be cited as typical. A recent adaptation of the Cottrell process has been for the removal of fly ash from the stack gases of boiler plants fired with powdered coal.



Courtesy of the Dust Recovering and Conveying Company

Figure 3—Elevation of Grinding Unit with Dust Recovery System

Cyclone separator and air filter in series eliminate dust and provide 99.5 per cent recovery of fines from ball mill. Cyclone separator handles larger particles and partially cools gas stream. Air filter removes fine dust not trapped by cyclone separator. Thermostatic control of emergency atmospheric air inlet prevents overheating of cloth filters.

Filtration of gas streams for the removal of dust was first practiced on a large scale in the smelting industry, which developed the baghouse, the now obsolete progenitor of the modern air filter. Some modern filters still use the baghouse system of positive pressure—that is, the forcing of dust-carrying gas through a filter medium against the pressure of the atmosphere. The air filter on the housewife's vacuum cleaner is a homely example of this type of filter. Industrial filters of this type, however, are open to the serious objection that the fan pushing the gas stream through the filter must handle dusty air. Where the dust is abrasive, the life of the fan is liable to be uneconomically brief. In other cases, where dust of a combustible nature is to be handled, the use of a fan on the dust-carrying air stream introduces a serious explosion hazard.

The objections to the pressure type of air filter have been met by placing the fan on the clean-air side of the filter and using it as an exhauster rather than as a pusher. Practically all industrial air filters are of this vacuum type. They are built in two chief styles. The first is adapted from the plate-and-frame filter press used for the filtration of liquids, and uses a large number of cloth-covered wooden frames set up tightly within a metal shell and dividing this shell into two compartments, one for the admission of dusty air and the periodic removal of the dust collected by the filter frames, the other for the removal of filtered air.

The frame style of vacuum air filter is not used so extensively as is the stocking type, in which the filter medium consists of a number of cylinders of filter cloth mounted vertically within a cylindrical metal shell ending in a cone bottom. These filter cloth cylinders are open only at the bottoms, which are attached to holes in the lower sheet of the cylindrical shell. Dusty air is introduced within the cone bottom below this lower sheet, passes up within the cylindrical filter stockings, which retain the dust and allow clean air to pass into the body of the shell, from which it is exhausted by a fan. The dust collected within the filter stockings is removed periodically by automatic shaking, accompanied by cut-off of the incoming dusty air, and in many cases by the blowing of air through the filter stockings in a direction reversed from that of filtration. The dust shaken from the filters settles into the cone bottom, from which it may be removed as desired through discharge gates or by a continuous conveyor.

The use of cloth filters imposes a temperature limit on the gas stream. The maximum allowable value for cotton filters is 95° C. or 200° F. This limit can be raised slightly if wool cloth is substituted for cotton, but even then the temperature must not exceed 115° C. or 240° F. Another factor that must be carefully controlled is humidity, since condensation of water from the gas stream upon the filters may completely upset their operation by clogging. The linear air velocity across the filter cloth area is variable, depending upon the characteristics and amount of material to be removed, but generally varies between 2.5 and 10 feet per second.

It is obvious that none of the air filters described can be operated continuously. The optimum cycle of operation depends largely upon the concentration of suspended material in the gas stream, upon the particle size, and upon the tendency of the particles to cohere and thus build up a resistance to gas flow. A filter might, for instance, operate satisfactorily for eight hours upon fine silica dust in the effluent air from a cyclone separator, but develop high resistance in thirty minutes upon gas black. In order to obtain the equivalent of continuous operation, it is necessary to use two or more filter units in parallel, so that while one unit of a group is cut out for cleaning filtration may still be carried on. Since, for any given set of conditions, efficient filtration depends largely upon the velocity at which the gas stream passes through the filter, it is important that this velocity be held as nearly constant as possible. This result can be approximated with increasing accuracy as the number of filter units in parallel is increased. One very excellent installation handling the dust from tumbling barrels in a large foundry uses groups of ten filter units each.

Utilization of Dust Recovery Equipment as a Unit Process

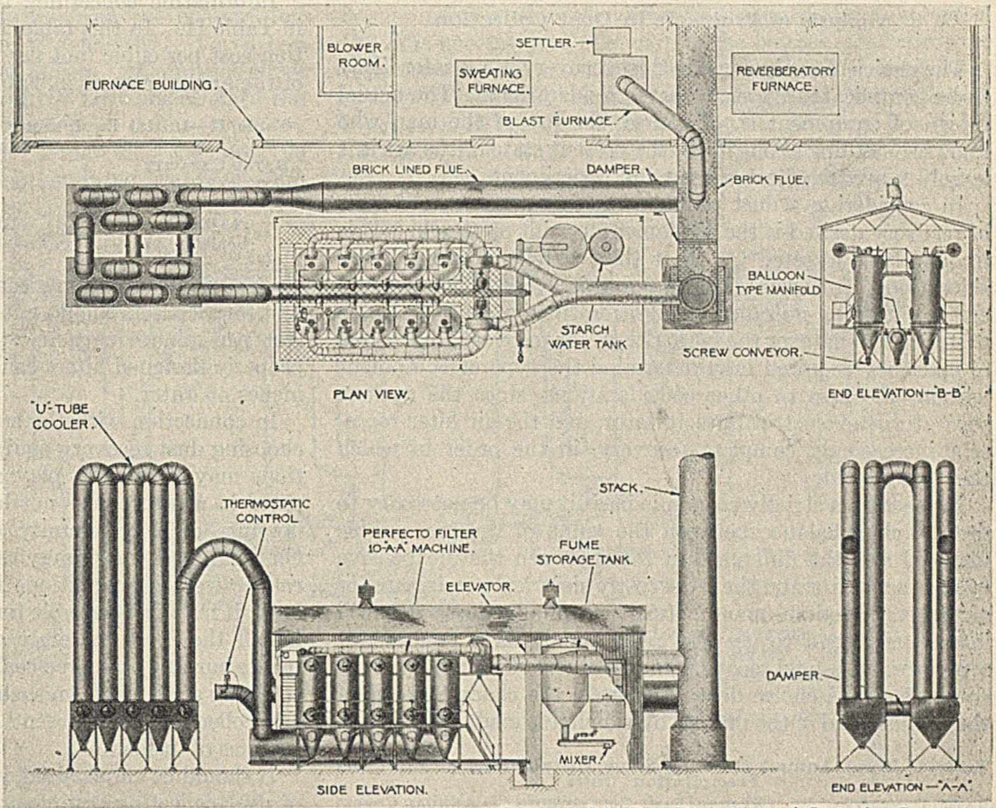
The possibilities latent in the field of dust collection are only beginning to be realized. Industry in general still holds the second attitude mentioned at the beginning of this article, that of controlling dust because it is a nuisance or a hazard or an economic loss. Thus we have equipment applied to the collection of dust from the operations of mixing, crushing, grinding, drying, and packing, generally only with the thought of preventing the waste or contamination of material. In certain cases, however, imaginative engineers have expanded the function of apparatus for dust collection until it takes new rank as a unit process.

One of the first developments of dust collection as a necessary integral part of a manufacturing process was in the production of gas black. The old, cumbersome, inefficient method of obtaining this material by deposition on metal plates hung over open gas burners, with subsequent scraping to remove the product, could be replaced by a compact, continuous burner of high efficiency only if some way could be devised for separating the elusive product from the stream of burned gas. Owing to the extreme fineness of the particles, filtration seemed the only possible solution. The first installation in this country was built to filter the gas while hot, and consisted of an ordinary unit of the vacuum type in which the cloth filter stockings were replaced by cylinders of monel-metal filter screen. This filter screen was not intended as the actual filtering medium, however, but merely as the foundation for it. Owing to the coherence of the particles, the gas black itself built up an efficient filter layer on the screens. Cleaning was accomplished by pistons, which moved vertically within the cylinders at intervals and scraped off all of the deposited material in excess of a certain thickness which was left permanently on the filter. This installation has been in operation six years. Since it was designed it has been found practicable to cool the gases leaving the burner to a point at which cloth filters may be used, and a gas black plant has recently been put in operation with this type of equipment.

Another field in which dust collection has become a standard unit process is the manufacture of dried milk. Here the function of the air filter is to remove all of the powdered product from the air stream leaving the drier. Since this air stream contains a considerable amount of moisture, it cannot be returned through the system, and a relatively large amount of air must be filtered. The dried milk removed by the filter is returned to the shell of the drier on a continuous conveyor, the final product being removed from the bottom of the drier.

In grinding operations giving a very fine product, the air filter again serves as a valuable unit, since it retains all of the fines, while preliminary removal of coarser particles may be effected by a cyclone separator operated in closed circuit with the grinding or pulverizing equipment. By tapping off a portion of the effluent air from a cyclone separator to an air filter in this way, it has been possible to produce bone black consistently finer than 350 mesh without loss of material.

The air filter again serves as an indispensable adjunct in cases where pneumatic conveying is applied to materials that dust readily. In some installations—for instance, in handling grain—it is desirable to separate the dust developed during handling, while in others—for example, the transfer of finished cement—it is imperative that all the fines be retained in the product. The first situation may be met by using a cyclone and an air filter in series with separate discharge, while for the second situation the same equipment would be used with a common discharge. In either case the cyclone is necessary to handle the bulk of the load and separate the larger particles, while the filter is necessary to capture the fines, whether nuisance or values, which are carried through the cyclone.



Courtesy of the Dust Recovering and Conveying Company

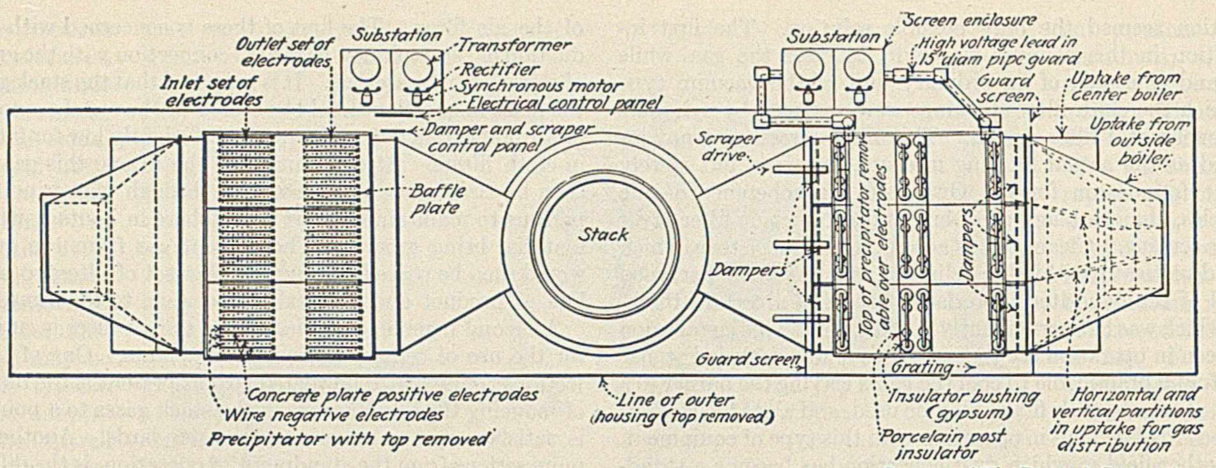
Figure 4—Layout of Metal Oxide Recovery System

Furnace gases carrying oxide fumes pass through coolers to air filters where oxide is completely removed, eliminating nuisance and recovering valuable material. Thermostatic control of emergency atmospheric air inlet prevents overheating of cloth filters. Vertical U-tube coolers require little space.

Proposed Applications of Air Filters

Two new developments, not yet applied commercially but deserving consideration, have been suggested in the application of the air filter. The first of these is concerned with the reduction of the explosion hazard in connection with the grinding of combustible materials. It is proposed that the stack gases of the plant in question should be cooled by the use of economizers or air preheaters to a temperature sufficiently low for filtration in cloth filters. After cleaning in the filters, this gas would then be circulated at a slow rate through the grinding apparatus to maintain an inert atmosphere in contact with the material being ground. The effluent gas from the grinders would then be passed through another set of filters to prevent loss of product and then exhausted clean to the atmosphere.

A second ingenious application of the air filter is suggested for the use of central-station power plants. One of the objections to the use of powdered coal at present is the difficulty of reducing the ash nuisance in the stack gases to a point that is satisfactory for modern urban standards. Another one, more serious from the standpoint of operation, is the difficulty encountered in pulverizing coal that is wet, owing to its tendency to ball up in the grinders. It is proposed to overcome both of these objectionable features by the use of air filters. Stack gases, carrying a large percentage of the total ash produced in the combustion of the powdered fuel, must first be cooled by the use of economizers and air preheaters to a temperature that will allow the use of cloth filters. The ash would then be completely removed in these filters, and the cleaned stack gas would be passed through the coal pulverizers, where it would serve the double purpose of preventing explosion and drying the coal during grinding. The gas from the pulverizers would be filtered again to retain powdered coal, and would finally be exhausted to the atmosphere in a thoroughly clean condition. One of the problems in the development of such a scheme would be the maintenance of the gas stream above the condensation point, since all the combined water of the coal, plus the water produced by com-



Courtesy of The Research Corporation

Figure 5—Plan of Plate-Type Electrical Precipitation Unit Used for Removal of Ash Dust from Stack Gases

Units of this type give 90 per cent recovery of the fly ash from the stack gases of a large centra station using boilers of 2000 to 3000 rated horsepower driven at 200 to 300 per cent of rating and fired with powdered fuel.

bustion of its net hydrogen, plus the moisture removed in drying, must pass the second filter and must do so at a temperature above the dew point to prevent clogging of the filter. The air filter in entering this field will have to compete with the electrical precipitation process, which has already been adapted to the removal of fly ash from powdered-fuel boiler installations.

Analysis of Problems in Dust Collection

The choice of equipment for dust recovery is a matter likely to be complicated by secondary considerations. The actual design of equipment is, of course, the job of the man who knows something about it; in the present state of the art it is largely a matter of experience and experiment.

In considering a dust problem the factor of completeness of recovery desired is the fundamental point of attack. This frequently is affected by other than strictly economic considerations; for example, lead oxide is a health hazard and cement dust is a nuisance, in addition to any loss of valuable material. Whatever the basic reason for recovery, the degree of efficiency required may determine the type of equipment without recourse to other considerations, since the cyclone separator, the electrical precipitator, and the air filter represent increasingly complete recovery, in the order in which they are named.

In cases on a strictly economic basis it may be necessary to draw a close balance between the value of the recoverable material and the difference in cost between the inexpensive cyclone separator and the more costly electrical precipitator or air filter. Modern manufacturing methods, however, will increasingly tend to use the cyclone only as a preliminary separator, with final recovery in one of the other two types of equipment, the choice depending upon the characteristics of the product and of the process by which it is made.

Table I—Total Annual Cost for Some Installations of Electrical Precipitation Units

Rated Capacity	Kind of Dust Collected	Annual Cost per cu. ft./min.
Cu. ft./min.		
1,500	Non-corrosive dust	$0.33
20,000	Valuable dust from polishing operations	0.20
70,000	Precious-metal dust from refining operations	0.076
500,000	Ash dust	0.06

Although it is impossible to lay down general cost figures for dust recovery equipment, owing to the wide diversity in the requirements of individual installations, some data of specific units of various capacities have been made available to the writer. Table I shows the data for four installations of Cottrell electrical precipitators. The figures for annual cost per cubic foot per minute capacity include interest and depreciation on the installation cost, power for operation, repairs and renewals, and a small allowance for labor, which with the Cottrell precipitator has been found to be nominal. As has been stated before, the power requirement for electrical precipitators varies between 5 and 10 kilowatt-hours and the repair costs are low.

Information concerning three filter installations is shown in Table II. In this table, however, only the actual installation cost per cubic foot per minute capacity is given, instead of the annual cost as in Table I.

Table II—Initial Equipment Cost for Some Filter Installations

Rated Capacity	Kind of Dust Collected	Initial Cost per cu. ft./min.
Cu. ft./min.		
12,000	Powdered milk	$0.80
15,000	Ash dust	0.50
400,000	Zinc oxide	0.50

Under proper operating conditions the annual replacement cost for air filters should not exceed $10 to $20 per 1000 cubic feet per minute capacity. The power cost is small, since properly designed filters cause a pressure drop of only 2 to 3 inches of water.

In connection with the economic aspect of the problem of choosing dust recovery equipment, the matter of local conditions may frequently play an important part. A plant located in a desert does not have to worry about the pending lawsuits of a community outraged by its dust nuisance. On the other hand, it may have to provide extraordinarily excellent working conditions in order to obtain labor. Similarly, it may be profitable for a public utilities corporation to install the most elaborate equipment for dust recovery on plants burning powdered coal, simply because of the intangible return in good will from such a public policy, even though the ash collected is at present a waste material with no great promise of utilization.

It should be emphasized, in conclusion, that the application of dust-collecting equipment to any specific process is more than a problem in sheet-metal construction and more than a problem that can be solved painlessly by the installation of two or ten or a hundred units of a perfectly standardized apparatus built to satisfactorily fit all conditions. In the present state of the art the engineer in the field of dust recovery is a specialist selling consulting service rather than selling cyclones, or air filters, or electrical precipitators. The firm which insists on buying equipment rather than such consulting service is liable to discover the old truth that the best apparatus in the world will not perform efficiently under conditions for which it was not intended.

Acknowledgment

The writer wishes to indicate his indebtedness to F. L. Jorgensen, of the Dust Recovering and Conveying Company, Cleveland, Ohio, for information concerning air filters and their application, and to The Research Corporation, New York, N. Y., for data on electrical precipitation.

Evaporation[1]

Philip De Wolf

Joubert & Goslin Machine & Foundry Co., New York, N. Y.

"EVAPORATION," used in the sense that the chemical industry applies it, means the boiling off of water, and water alone, from a solution containing water. If anything but water is boiled off, the operation is called "distillation"—the dividing line being so drawn for no better reason than that it has always been so drawn.

This evaporation may be done by heating a liquid in a kettle over a fire, by passing hot gases over the liquid in a flat pan, by passing hot gases up a tower while the liquid runs down, by spraying from the periphery of a rapidly revolving disk through hot gases, or by exposing to the sun. All these methods find legitimate application in the chemical industry. However, most of the evaporation in industry is done in closed vessels, which hold the liquid, the heat being applied through a steam coil or some modification of it, immersed in the liquid, and the vapors resulting from the evaporation being taken away to some form of condenser. To such a machine the term "evaporator" is applied. In multiple effect the condenser is the heating coil of the next vessel, until the last one, which is an actual condenser.

Such a series takes advantage of the facts that the lower the pressure the lower is the boiling point and that heat flows from the warmer to the colder object. The condenser creates a high vacuum (or low pressure) in the last "effect," as each vessel is called, and the liquor therein boils at a correspondingly low temperature. Vapor at a higher temperature and pressure comes into the steam chest of the last effect from the boiling liquor in the next to the last effect; it is condensed and its latent heat passes through the steam-chest walls and boils the liquor in the last effect. It is necessary, of course, to have the heating vapor enough hotter than the liquor to be boiled to do the job economically, and that is one of the most important features of design. Inasmuch as the limitation of space precludes doing justice to the subject of heat transfer in this connection, this paper will be confined to descriptions of operating conditions, and their effect upon design, for the local conditions do not in any way affect the fundamental conditions.

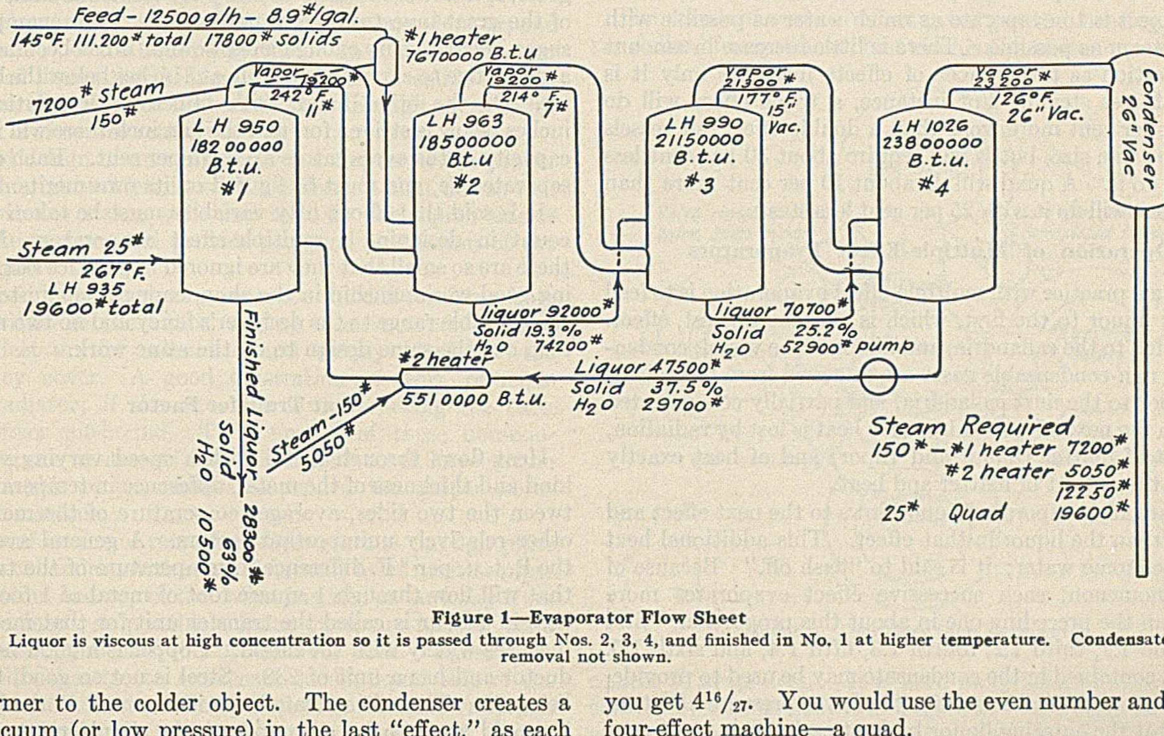


Figure 1—Evaporator Flow Sheet

Liquor is viscous at high concentration so it is passed through Nos. 2, 3, 4, and finished in No. 1 at higher temperature. Condensate removal not shown.

Principle of Operation

Boiling points of solutions vary at different concentrations. This and other factors must be worked out and, in addition to the heat necessary to take care of them, the heating vapors must be 15° F. higher than the liquor, to insure a good boil. So, assuming in the case under discussion that an average of 12° F. is necessary to take care of the factors mentioned, the vapor coming to each steam chest (or callandria) must be at least 27° F. higher than the vapor from the liquor it is to boil. If you have 10 pounds of steam at 240° F., and your condenser runs at 27 inches, for which the temperature is 116° F., you have an over-all heat drop of 124° F. Divide this by 27, and you get $4^{16}/_{27}$. You would use the even number and install a four-effect machine—a quad.

Figure 1 shows a typical layout, with the temperatures and pressures of the vapors and liquids.

The whole point is that the heating steam is condensed on the wall of the callandria, which is kept cool enough to do this by the liquor to be evaporated, and in condensing gives up its latent heat. This latent heat and the sensible heat due to

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[1] Received February 9, 1929.

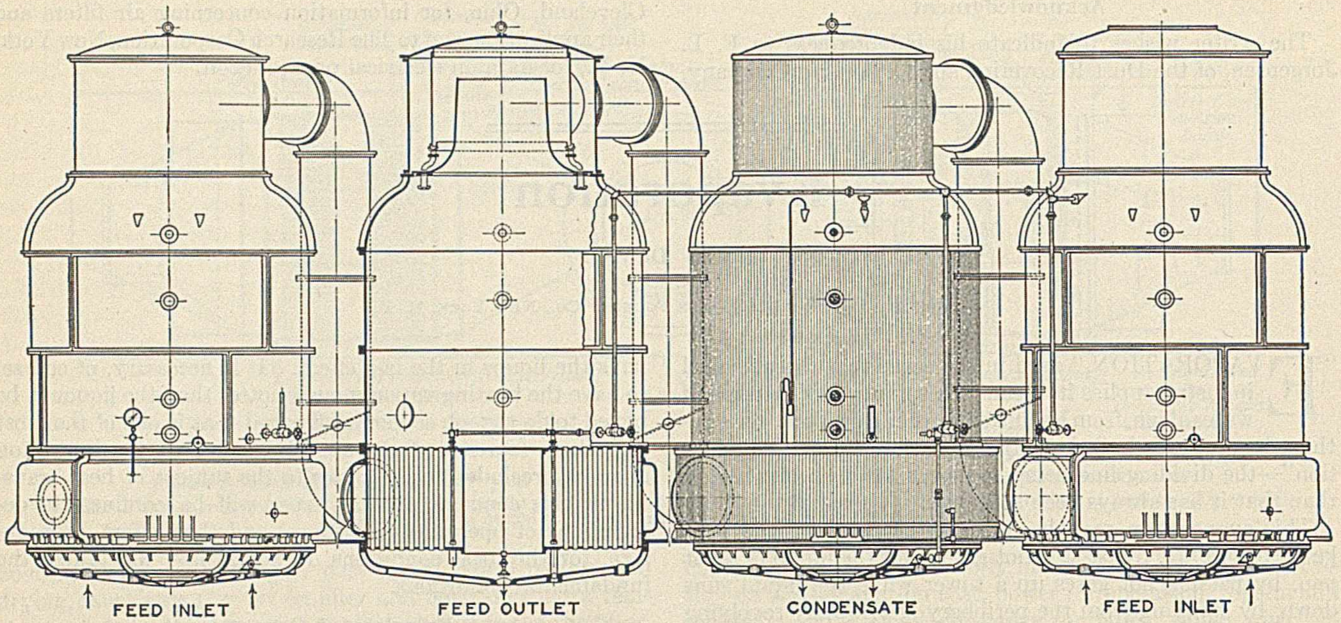

Figure 2—Standard Vertical-Effect Evaporators*

the higher temperature on that side pass through the wall and are sufficient to boil the liquor which, because of the lower pressure in that side, has a lower boiling point than the just condensed vapor. Actually the latent heat is moved along, vaporizing water, being carried over into the next callandria, given up when the vapor condenses, through to new liquor and repeated.

As the latent heat increases with each drop in boiling point, a little of the sensible heat has to go in just to help boil the liquor—to make up its full quota of latent heat.

The object is to evaporate as much water as possible with as little steam as possible. There is little increase in amount of evaporation as the number of effects increases only it is done with less steam. For instance, a triple effect will do about 15 per cent more work than a double effect, all vessels being the same size, but it will require about 30 per cent less steam to do it. A quad will do about 10 per cent more than a triple, but will do it with 25 per cent less steam.

Operation of Multiple-Effect Evaporators

The usual practice with multiple-effect evaporation is to feed the weak liquor to the first, which is also the hottest, effect. Steam is fed to the callandria, and liquor to the vessel; condensate and non-condensable gases are removed from the callandria; vapor to the next callandria, and partially concentrated liquor, to the next effect. Also some heat is lost by radiation, the input of matter (liquor and vapor) and of heat exactly balances the output of matter and heat.

The partially evaporated liquor flows to the next effect and is hotter than the liquor in that effect. This additional heat evaporates some water; it is said to "flash off." Because of this phenomenon, each successive effect evaporates more water than the preceding one in about this proportion: first 1.0, second 1.1, third 1.2, fourth 1.3, fifth 1.4, and sixth 1.5. The heat contained in the condensate may be used to provide, by flashing, additional vapor for the lower pressure effect, or it may heat the entering liquor by heat exchangers, or it may go to the plant process water.

The above does not, of course, apply to single-effect evaporators, but they are only used where a difficult boiling condition arises and steam economy is not the most important factor.

Design of Multiple-Effect Evaporators

Multiple-effect evaporators may have from two to any practicable number of effects. Twelve is the largest number the writer has ever heard of, and that was on a ship with 300 pounds of steam available to make distilled water from sea water. The vacuum maintained in this condenser, of course, will influence the number of vessels. When evaporating liquors that give off a considerable amount of non-condensable gases, it is not economical to carry too low a vacuum, because of the great investment and power costs. For example, raw sugar juices give up enough gases so that it has become standard practice to carry the vacuum at 3 inches below the barometer. On the other hand, with mineral salt solutions $1^1/_2$ inches below is striven for, and the last inch there will increase capacity of the evaporators up to 15 per cent. Each case is a separate one, and must be figured on its own merits.

It is said that about fifty variables must be taken into account in designing a multiple-effect evaporator. Most of these are so small that they are ignored in practice but, assuming good workmanship in the shop, enough remain to permit considerable range to the designer's fancy and no two men will turn out the same design to do the same work.

Heat Transfer Factor

Heat flows through metal with a speed varying with the kind and thickness of the metal, difference in temperature between the two sides, average temperature of the metal, and other relatively unimportant factors. A general average of the B. t. u. per ° F. difference in temperature of the two sides that will flow through 1 square foot of metal of 1 foot thickness in 1 hour is called the transfer unit for that metal, and it varies widely with the metal. Copper is a good heat conductor and has a unit of 238. Steel is not so good, the unit being 25. These heat transfer units are well worked out, so it would seem to be a comparatively simple matter to figure the size machine to transfer (or transmit) the heat required.

But an evaporator has liquid on one side of the dividing wall and either vapor (steam) or liquid (condensed steam) on the other. On the metal surface is a film of the liquid or vapor and the heat passes into this film on the hot side, through it to

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* Figures 2 and 8, reprinted from "Evaporation," by Webre and Robinson, published by the Chemical Catalog Co., Inc.

the metal, through the metal to the film on the cool side, through it, and then into the liquid to be heated. Much research remains to be done, but we know that the heat transfer is very slow through this combination—so much slower than through the metal alone that the heat transfer factor of the metal is really a small item. For example, in an evaporator for salt brine, with copper tubes, the over-all heat transfer unit will be about 1, which is 4 per cent of the straight steel and about 0.42 per cent of the unit for copper.

While this heat transfer factor is made up of the combined resistance to flow of the two films, the metal wall, and the boundary planes between them, nowhere near enough work has been done on the separate films. Evaporators are designed on data worked out from actual practice, the unit being a pound of water per square foot heating surface per hour evaporated under such conditions.

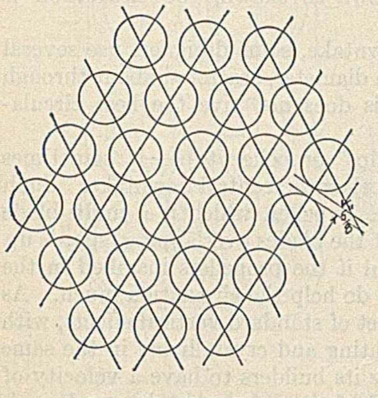


Figure 3—Tube Layout

The metal wall does not change except as it may corrode, but the films change rapidly, and their changes affect profoundly the flow of heat. On the steam side the top of the tubes in a machine with vertical tubes has little liquid on it—only the condensate from the steam condensed there. But as you go down the tube there is the steam condensed at any certain place plus the water that has run down from above. The path the steam takes through the callandria affects this film. Anything brought over by entrainment in the vapor may stick to the tubes.

On the liquor side crystals may form, dirt may deposit, and the rate of flow of the liquor may vary. In general, the faster the flow of liquor the thinner is the film. If solids are deposited on the wall, the heat must pass through these solids also, and is of course retarded.

So good design of an evaporator is a matter of the proper size, of the right materials, with a callandria that drains well and distributes steam well, and that on the liquor side is easy to keep clean and provide for good circulation of the boiling liquor.

Air mixed with the steam, or carbon dioxide resulting from decomposition of the liquor, or any other non-condensable gases collect in the callandria and simply blank off the space they cover. A good illustration of this principle is in a radiator; if the air valve is not working the back end becomes air-bound. The removal of these non-condensable gases is always important, and cases have arisen whereupon this proper removal depended the proper working of the machine.

The usual means of removing these gases is through pipes inside the callandria, with small ($^1/_{16}$ inch) holes in these pipes at the bottom and top of the callandria and as far away from the steam inlets as possible. Some gases are heavier than steam, some lighter, and this provides for both. These pipes are carried either to the condenser or the liquor side of the same effect. The latter is bad practice, as the same vapors go into each callandria in turn and have to be removed, and as the volume increases with the drop in pressure they may be a serious matter in the last effect. All that can be saved by this method is a little piping, and it will not pay.

Any well-designed evaporator, of any recognized type, will transfer the same amount of heat per unit area, provided the conditions, such as cleanliness of surface, circulation, temperatures, and pressures, are the same. So the type of machine must depend upon conditions existing; every evaporator job is a separate engineering problem.

The two greatest factors for economy are the amount of steam used on the job and the cost of apparatus, always assuming good engineering practice such as choice of materials and shop work.

The operator can make or mar the performance of an evaporator, however. It is usual practice to figure that a quad on raw sugar juice will evaporate 6 pounds of water per square foot per hour. This company built a quad that is installed in the mountains in Cuba, where the barometer is a little below that at sea level, and this quad has been running for several years at an average rate of 10.5 pounds per square foot per hour, or 75 per cent overload. It is needless to say that the operation there is excellent.

Coil as Heating Element

The simplest heating element is a coil of pipe, with the steam inside. The milk evaporators are the only ones now using this design to any extent, although in other industries—sugar, for instance—a coil is sometimes added to another type of machine to give some additional heating surface. The objections are many. If many coils are used, the circulation of the liquor is not good, and the coils are hard to clean. If the coils are few and small, the heating surface and the capacity are cut down. In any event, the lower end of the coil is always too full of condensed steam that has run down from above to do good work. It is difficult to remove the non-condensable gases properly. The coils are supported upon brackets that provide small recesses from which dirt is difficult to remove; in the case of foodstuffs, such as milk or sugar, this dirt may be bacteria.

Vertical-Effect Evaporators

The standard vertical effect gives greatest heating surface per dollar of investment, best circulation of liquor, and is the easiest to keep clean. It is used more than all others. Its construction is as shown in Figure 2. The body is built of cast-iron, sometimes steel, flanged rings, or belts, which are bolted at the flanges. For very large machines these belts have to be made in several pieces, so the railroads can handle them, joints are always to be avoided as they are potential leaks. It is unusual to ship any belts, even up to 10 feet inside diameter, all in one piece, although it is sometimes accomplished.

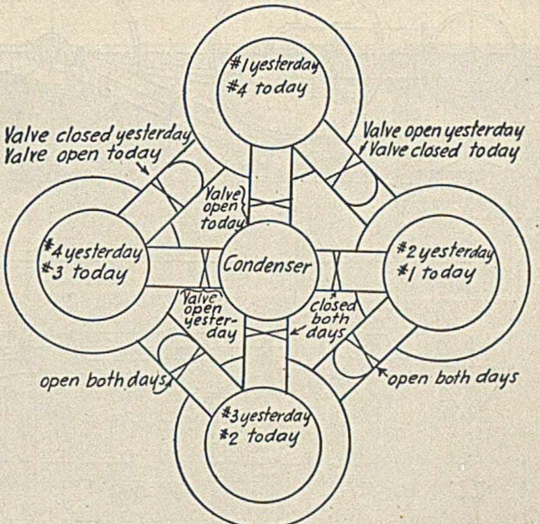


Figure 4—Distillery Slop Evaporator

The 13-foot inside diameter quadruple effect built for the Gulf States Paper Company, at Tuscaloosa, Ala., has rings all in one piece, some being 8 feet from face to face of flanges. Such an evaporator holds its vacuum well. The upper and lower tube sheets are bolted between the flanges of the steam belt and adjoining sections, the center downtake welded or riveted to these sheets, and the tubes expanded at each end into the sheets. The circulation is up through the tubes, where heat from the steam on the outside of the tubes is absorbed; the vapors rise and pass through the vapor line to the next effect, and the unevaporated liquor flows over the tube sheet to, and then down, the center downtake. When cold, the liquor stands about two-thirds of the way up the tubes when a 4-foot long tube is used; when running, the liquor should cover the tube sheet, no two liquors or two evaporators work best with identical conditions.

To get the maximum heating area, the tube sheets are drilled to the outside size of the tube plus $^1/_{64}$ inch, the holes being centered on a pattern of equilateral triangles, with sides the size of the tube plus $^5/_8$ inch. (Figure 3) The smaller the tubes the greater number can be used, and the heating surface goes up until about $1^5/_8$-inch tube is reached. (Figure 3) Smaller than that the $^5/_8$-inch bridge wall is out of all proportion and there is a loss in area. So for free circulating liquors that do not dirty the tubes too much, $1^3/_4$ inches o. d. seamless drawn tubing is used; gage will run from 14 to 17 gage, depending upon the material and other conditions. For steel, 16-gage is a good average. Where crystals form easily or other forms of matter are likely to stop up the tubes, up to 4-inch tubes are used. Examples are the concentrators for caustic soda and the final effects and concentrators for sugar. As salt (NaCl) is crystallized out in each effect, because the operation is started with a saturated solution, and it begins to crystallize out as soon as any water is removed, $3^1/_2$ or 4 inches is the usual size of tube in that industry.

The longer the tube the greater is the area. The friction is also greater, and when the tubes are really long the weight of the column of liquor, the static head, becomes a factor. So tube length is determined by experience. The standard machine for raw sugar juices has copper tubes, 16 or 17 gage, $1^3/_4$ inches by 4 feet.

The downtake size is also determined by experience. A 4-foot diameter (always inside diameter) would have an 18-inch downtake. But in the larger sizes it is not the area of the downtake, but the length from wall to downtake, that determines its size. It can be taken as a safe rule that the distance from inside of shell to downtake must not be over 5 feet 6 inches, or the circulation will not be good. If the central downtake is continued down as shown, the circulation is considerably improved.

Instead of a central downtake, some designers use several large tubes 4 or 6 inches in diameter, scattered about through their smaller tubes. This does not give the best circulation.

A propeller—regular ships' propeller type—is sometimes installed either in or just below the central downtake. Such a design as a Woods type impeller, which is a multi-blade propeller with the edges of the blades overlapping, speeds up circulation. It is doubtful if the propellers installed in the space below the downtake do help the circulation much. As an illustration, one large set of standard vertical effects, with a propeller below, evaporating and crystallizing in the same effects, was guaranteed by its builders to have a velocity of liquor through the tubes of 6 feet per second; the purchaser's engineers found it to about 6 inches per second not much over 8 per cent of the guarantee. The propeller had its uses, however, for it kept the liquor sufficiently agitated to keep the

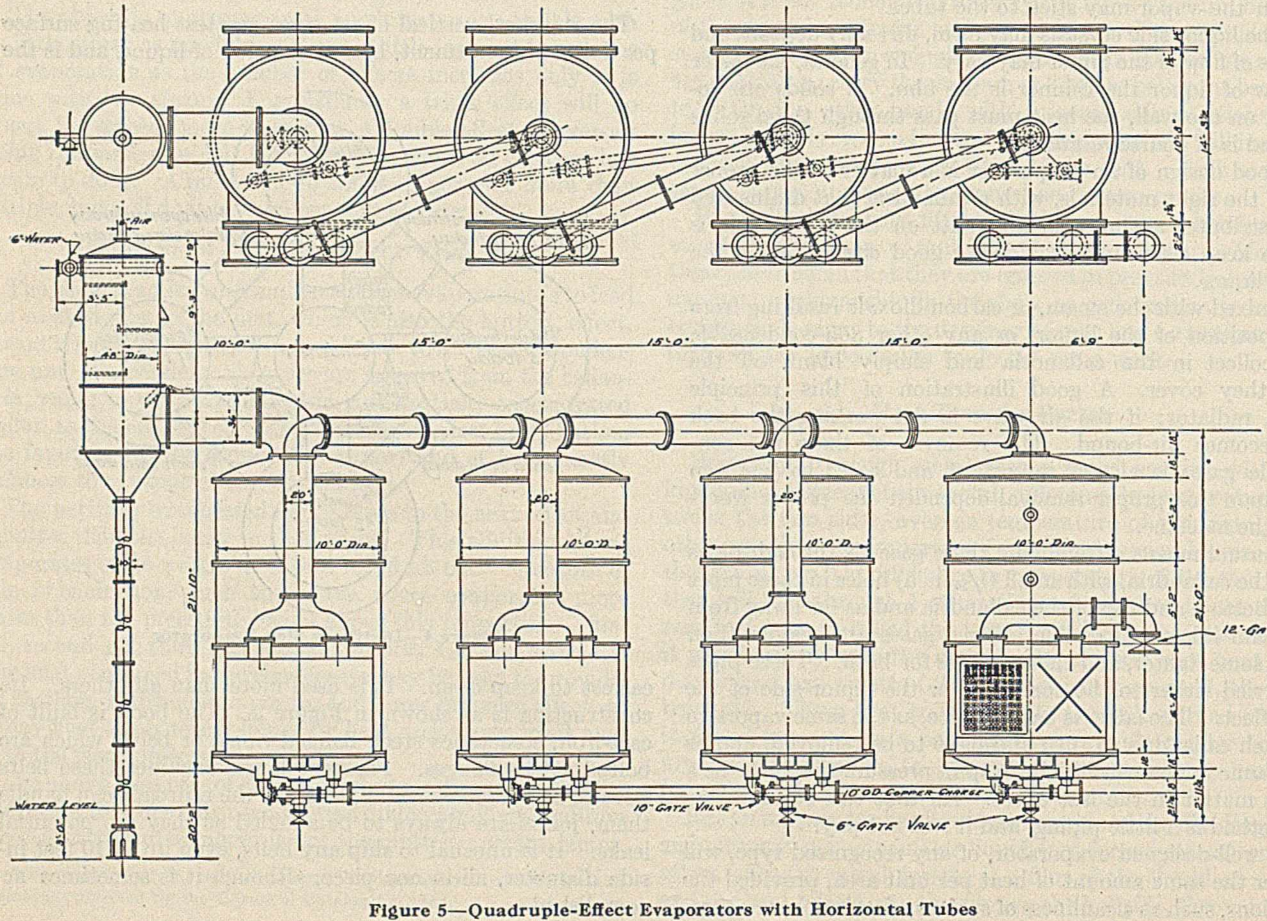


Figure 5—Quadruple-Effect Evaporators with Horizontal Tubes

small crystals in suspension until they could grow; when they became large enough they settled out.

For one particular condition that the writer has worked upon, a velocity through the tubes of 3 feet 6 inches per second is sufficient to prevent any large quantity of crystal formation inside the tube, thus insuring clean tubes and a good rate of heat transfer. But the figure will vary, and can only be found for each set of conditions by direct experiment.

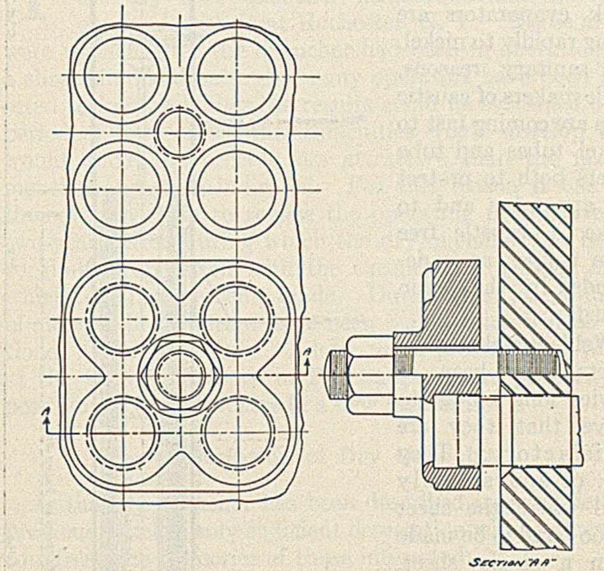


Figure 6—Method of Holding Tubes in Horizontal Effect

An evaporator to handle distillery slop had to contend with a deposit on the tubes of the first effect sufficient to almost stop circulation in 48 hours. This deposit was easily soluble, however, in the strong liquor of the fourth effect. So the four effects were set at the corners of a square, instead of in a straight line as usual, and the condenser was put in the middle, connecting and valving the vapor piping so that any effect might be used as No. 1. The operation developed, and still in use after about fifteen years, is to run 24 hours and then shift valves so that No. 1 becomes No. 4, and the strong liquor cleans the tubes; what was No. 2 becomes No. 1, the other two effects are changed to correspond, and it runs well another 24 hours. Figure 4 will make the layout clear.

To clean tubes in the standard vertical effect, a man stands on the top tube sheet and works down with a stiff brush or any other kind of tube cleaner. A brush will not always do it, however. In salt evaporation, where the gypsum precipitates out, the tubes must be drilled out with an air drill. In sugar it is necessary to boil out with caustic soda every week or so. No matter what boiling out must be done, the standard vertical-effect arrangement of tubes is the most accessible of any so far devised.

The subject of forced circulation is still controversial. A lot of power is required, and only experiment can show whether it will pay in any given case.

Basket-Type Callandria

The basket-type callandria has its tube sheets forming the ends of a cylinder, the tubes being expanded into each one as in the standard effect. There is no central downtake, as when the basket is hung by brackets in the effect a ring is left between the basket and the outer shell. Circulation through this ring is good. There are more joints which may leak than in the standard effect, and with usual proportions less heating surface. Therefore, the cost will be greater per unit. The operation is the same as the standard effect.

Horizontal-Tube Evaporators

In certain sulfate pulp mills it has been noticed that the tops of the tubes corrode very rapidly, from the steam side. Although the writer believes that this is due to the improper removal of gases, this fact is not yet established. Of course, a tube with the top 10 per cent gone is not much good, and must be entirely replaced. It is therefore thought to be economical to install horizontal tubes; the upper 10 per cent may then be eaten away and the lower 90 per cent not touched. There are many other conditions where a horizontal tube is required.

Figure 5 shows the general scheme. The ends of the tubes are not expanded into the tube sheets, but are held in place by rubber gaskets, and clamps, each clamp holding a nest of 4 to 8 tubes, and being bolted to the tube sheet. The tubes can be drawn out by removing the covers. (Figure 6)

If clean, this machine will evaporate as much water per unit of heating surface as the vertical, but it is difficult to clean, and as the circulation is none too good, it dirties up easily. The usual way of cleaning dirty tubes—that is, if the dirt is hard—is to remove them and tumble them in a rod mill.

Design capacity has been taxed to the limit to get as much area as possible in such a machine, as it is well below the vertical effects in this respect. The photograph (Figure 7) shows one effect of the machine for the Gulf States Paper Company, which has 6650 square feet of heating surface in a 13-foot machine—a very large amount. This has been achieved by widening the tube sheets to the limit of the steam chest, but still retaining good circulation.

Kestner Evaporator

The Kestner evaporator is a long-tube (22 to 24 feet) vertical machine, in which the liquor only stands 18 inches or so up in the tubes. (Figure 8) The long tube makes a flue up which the vapors race, carrying the unevaporated liquor by entrainment. Above the tubes is a baffle so arranged as to separate the vapor and entrained liquor, letting the vapor go to heat the next effect, the liquor draining into the liquor space of the next effect also. There is no downtake, as the liquor is passed through each effect only once, although the outside piping may be arranged so as to return the liquor for reëvaporation. Circulation is very rapid, and evaporation rate is high.

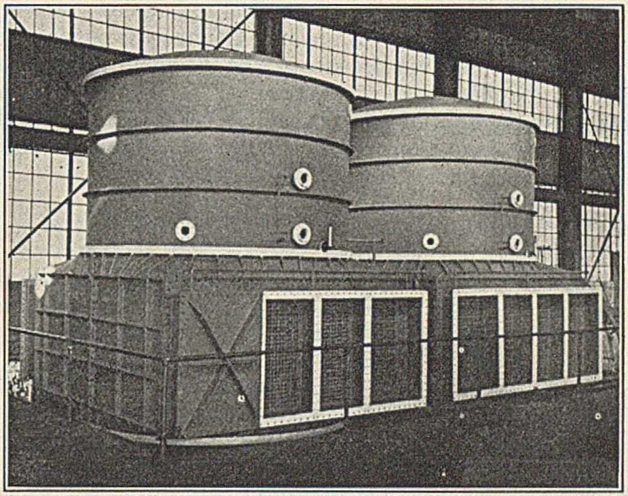
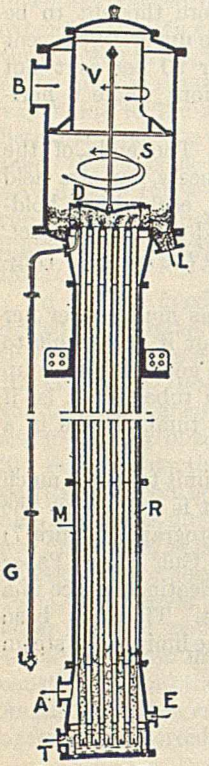


Figure 7—Two Effects of Horizontal-Tube Machine

Lille Evaporator

The Lille is a horizontal-tube machine, with tubes U-shaped and long. The liquor space is at one end of a cylinder, the one tube sheet holds both ends of the tube, and the other end of the cylinder is the steam space. In general the operations are similar to those in the Kestner, only part of the tube being full of liquor.



Courtesy of Kestner Evaporator Company

Figure 8—Kestner Single-Effect Evaporator

New Designs

Two new designs have come out recently, the effort being in each case, to increase the rate of circulation, with its cutting down of deposits of solids and thinning the film on the liquor side of the tube, thereby increasing the rate of evaporation.

One is a long tube machine with a pump below, as shown in Figure 9. The Swenson Evaporator Company made such a machine first, connecting the bottom of their basket to the outlet of the pump, and returning the overflow to the inlet. Such a machine is very effective for viscous liquors, ones that would not circulate by thermal circulation. It is used as a single effect, or as a finishing effect to a multiple effect, taking steam at 50 to 100 pounds, discharging its vapor to the first effect of the multiple, so having a high-temperature drop, and receiving its liquor from the last effect of the multiple. It is, as the name implies, a "high concentrator," and a good one.

An illustration of its usefulness is in a kraft paper mill, where it concentrated the black liquor much higher than any other machine could, thus sending a fuel to the black liquor furnaces that is much more economical to handle.

The Buffalo Foundry and Machine Company is putting out a long-tube vertical effect, but carrying the liquor level above the top tube sheet. The tubes are over 20 feet long, but the dreaded bogie of "static head" does not seem to interfere with the excellent circulation and general operation of this machine, which is run in multiple effect.

Materials Used

With the cheapening of nickel and alloys of iron, nickel, and chromium and more knowledge of heat-treating and fabricating them has come a great deal of good work on proper materials for evaporators. Sulfuric acid is still handled, not very satisfactorily, in either solid lead or lead-lined evaporators. Milk evaporators are going rapidly to nickel, for sanitary reasons, while makers of caustic soda are coming fast to nickel tubes and tube sheets both to protect the apparatus and to make a caustic free from copper, as is demanded by the rayon industry.

Welded nickel tube sheets have been in service long enough to prove that they are satisfactory. They are, of course, only used where the sheet is too large to be made from a single sheet. On complex liquors, like those of paper mills, it is increasingly the practice to put in a half dozen tubes of various alloys, and after a year or so take the tubes that have stood up best as standard. The difference in heat transfer factor for the various alloys can be neglected.

The fundamentals in multiple evaporation have not changed in eighty years, but the details have and each year sees better machines.

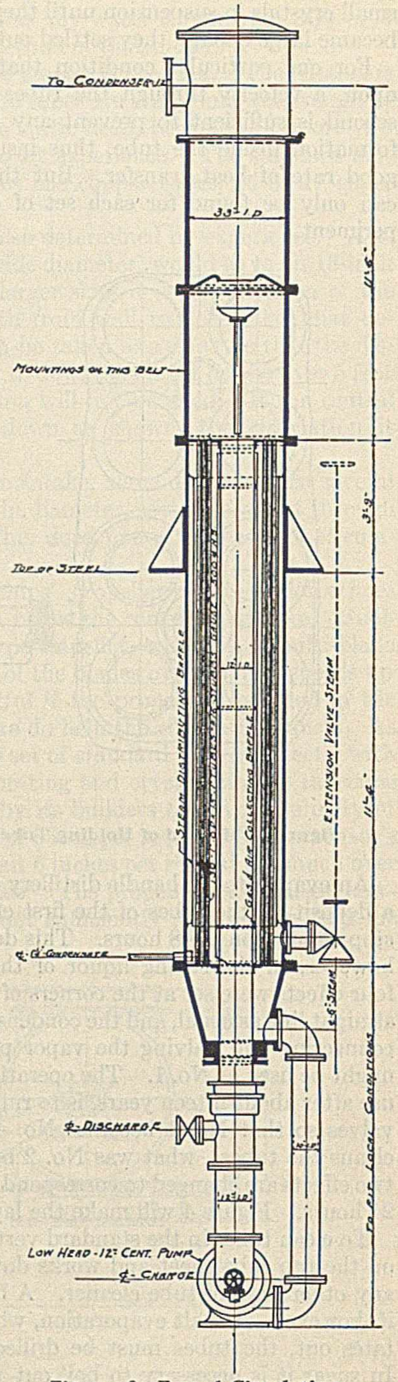


Figure 9—Forced-Circulation Concentrator

Paper Research at Bureau of Standards

The Paper Section of the Bureau of Standards has been investigating the permanence of paper, employing the standard age treatment (72 hours at 100° C.). One sample showed considerable change in alpha-cellulose content, copper number, and color. However, this paper appeared satisfactory from the standpoint of durability, but did not rate so high for permanence.

A report on the quality of purified wood fibers has been completed for presentation at the 1929 meeting of the Paper Technical Association. Commercial cornstalk papers made by the Kalamazoo Vegetable Products Company, composed of approximately 60 per cent cornstalk fiber and 40 per cent sulfite wood fibers, was examined and found to compare favorably with sulfite wood fiber papers, although containing specks which evidently were due to incomplete defibering of the stalks.

Considerable interest centers about the barrel tester for postage stamps, the object being to ascertain what proportions of stamps would become detached after very rough handling of the envelope. The barrel tester is to be used in connection with complaints regarding defective stamps, and if, with a standard method of affixing, the stamps are not shed from kraft envelopes in a test that wears out the envelope, the sticking qualities are not to be considered poor enough to justify complaint.

The section has also studied the Mullen tester to obtain the effect of the size of the aperture and the age of the rubber diaphragm upon its results. Other tests have been made on the Schopper folding tester, temperature tests on postage stamps, and on the official methods of certain technical associations.

Dry Quencher Operation at Rochester, N. Y.[1]

Frederick J. Pfluke[2]

Rochester Gas & Electric Corporation, Rochester, N. Y.

THERE have been published three articles describing the dry coke quencher installation and the results obtained with it at Rochester, N. Y.[3] These articles were written after the quencher had been in operation only a short time and naturally many operators have been interested to know whether the results could be sustained over a period of time or whether difficulties would develop which would make the process less attractive than the first six months' operation indicated. For this reason it has been thought advisable to review the operating results over the two-year period during which the dry quencher has been in continuous operation with the exception of periods during which repairs were being made. During this time a number of changes in operation have been made which will be mentioned at various points. A later paper presented by Wilson[4] at the Coal Conference in Pittsburgh covers primarily the possibilities of the process in a new installation.

Description of Dry Quencher

As the dry quencher has been described in great detail in previous articles, only sufficient description will be given here to refresh the memories of those interested.

Hot coke, as taken from the carbonizing unit, is dumped into a steel hoist bucket in the skip pit, as shown in the accompanying sketch. The bucket of hot coke is raised by a motor-driven cable hoist to the top of the hoist tower, where the hot coke is discharged into the top chute, through which the coke is guided to a steel brick-lined container of 40 tons capacity. A water-sealed door on the top of the container closes after the coke has entered the container. A fan, which is running continuously, draws the hot gases from the top of the container through the top boiler and the top section of the bottom boiler, back through the bottom section of the lower boiler where the heat is absorbed in producing steam, through a dust chamber where the dust is separated out, and into the fan. From the fan the gas is discharged through the gas duct into a gas distributor in the bottom of the coke container, which distributor diffuses the gas. It then passes through the hot coke, where it removes the sensible heat of the coke and then repeats the cycle. The container is kept full of coke, and just previous to the charging with hot coke enough cooled coke to make room for the hot load is withdrawn through a self-sealing gate and dumped on the wharf. The temperatures at the various points in the system are indicated on the sketch. There are two complete independent containers with fans and boilers, both charged by a single hoist car.

Circulating Gases

The medium of heat transfer is inert gas, chiefly nitrogen. It is not necessary to supply this gas, as the oxygen in the air, which is in the container at the start, is consumed very soon after the first hot load is introduced, leaving nitrogen and carbon dioxide. The system being practically air-tight, no appreciable loss of gas takes place. As far as can be determined, there is no loss of coke by combustion due to air infiltration while the quencher is in operation. The reason for this can be readily seen by referring to the sketch. The only points through which air can enter are at the discharge door and the charging door. Only one of these doors is open at once. The opening then becomes a point of zero pressure and theoretically nothing either enters or leaves the chamber. Actually there is a surging, swirling action at the point of opening at the top when charging, so that some air is drawn into the container. However, this small amount of air very desirably burns the volatile matter distilled from the coke which accumulates in the circulating gases instead of burning the coke. This combustion takes place before the boiler, thereby increasing steam production without any combustion of coke, as will be discussed later. This combustion takes place almost entirely at the top opening, as the bottom discharge door is open only a few seconds to discharge coke and the amount of air infiltration at this point is practically nothing. The possibilities of an explosive mixture in the container are very remote if carefully controlled, as has been brought out in the previous articles, and it should be sufficient to say here that at no time during the two years of operation has a dangerous condition been discovered, although there have been many varying conditions encountered, during which times the circulating gases have been carefully analyzed. Care in operation when starting up and shutting down, however, is very necessary to avoid possible dangers.

Under the operating conditions the circulating gases have the following average analyses as obtained from gas samples taken over a period of several days from the gas duct at the bottom of container:

CARBON DIOXIDE Per cent	OXYGEN Per cent	CARBON MONOXIDE Per cent	HYDROGEN Per cent
Before charging, at which time the coke is coolest			
13.0	0.6	5.0	Less than 10
During charging, top door open and maximum air infiltration			
14.3	0.6	1.7	Less than 10
After charging, doors closed tight			
10.9	0.37	6.6	Less than 10

Capacity and Steam Production

According to the guarantee made by the designers of the dry quencher, the capacity of the two units was 425 tons of coke per day, which was to produce 375 pounds of steam per 1000 pounds of coke of specified temperature, ash content, and breeze content. A test of 6 months' duration showed a steam production of 431 pounds per 1000 pounds of coke when running at the guaranteed rate. Immediately following the 6 months' test it was decided to attempt to put the entire coke production of 525 tons per day through the dry quencher. This was done and it was found that the 525 tons could be handled and the temperature of the coke discharged was only slightly increased. The steam production rate has actually been increased from 431 pounds to 506 pounds per 1000 pounds of coke. The increases in capacity and in steam production have been obtained as a result of the following changes:

(1) The gas circulation through each container has been increased from 17,000 to 21,000 cubic feet per minute by speeding up the fans. The fans are driven by variable speed motors and it is possible to obtain various circulation rates up to 21,000 cubic feet per minute maximum.

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[1] Received January 9, 1929.

[2] Assistant engineer.

[3] Beebee, *Gas Age-Record*, **59** (March, 1927); *Gas J.* (*Canada*), August, 1927; *Proc. Am. Soc. Mech. Eng.*, Fuel Division, October 10, 1927.

[4] Wilson, *Gas Age-Record*, **62** (November, 1928).

(2) It was found that owing to channeling some of the coke in the portion of the container over the discharge chute passed through the container twice as fast as the remainder. This resulted in some hot coke being discharged, which lowered the steam production. The difficulty was overcome by installing baffles in the discharge openings. As near as can be determined, all the coke now passes through the containers at a uniform rate and practically no red-hot coke is discharged.

(3) The largest increase in steam production is due to the burning of the combustible gases present in the circulating gases as a result of the distillation of any green coke entering the container which results from green ends or uncarbonized portions of a charge. The heat required for this distillation is supplied by the sensible heat of the coke. It has been found that the volatile in the dry-quenched coke is 0.5 to 1 per cent less than in the wet-quenched coke. That combustible gases are being distilled off the coke is proved by the fact that, if the top door of the container is closed as soon as the hot charge has been dumped, the hydrogen content of the circulating gases eventually builds up as high as 60 per cent. During the time the charging door of the container is open, this point becomes a point of zero pressure and a sort of swirling action takes place, causing air to be drawn in and some gases to be expelled. The air drawn in burns the hydrogen and the products of combustion are drawn through the boiler. This heat is then recovered in the form of steam. By delaying the closing of the top charging door of the container, therefore, the amount of air drawn into the container can be regulated to keep the combustible below 10 per cent, which makes operation safe and at the same time gives greater steam production. The analyses during this interval (given above) show that the oxygen drawn in is entirely consumed before it enters the boiler, and there is no increase in the oxygen content of the circulating gases entering the coke container so that coke combustion does not take place. It has been found at Rochester that the desired results are obtained by leaving the charging door open 80 seconds. This is accomplished automatically by a time-delay relay which can be set for any time delay desired.

It is interesting to see how the total heat recovered compares with the heat available in the coke. Coke enters the containers at 1780° F. and is discharged at 600° F.

	B. t. u.
Steam at 140 pounds pressure	1194
Heat in feed water	170
Heat from coke per pound steam	1024

1024 B. t. u. × 0.506 pound steam per pound coke = 518 B. t. u.

Radiation loss, 5 per cent

$$\frac{518 \text{ B. t. u.}}{0.95} = 544 \text{ B. t. u. total heat transferred from coke}$$

Available heat in Rochester coke between 1780° and 600° = 478 B. t. u. per pound coke

544 B. t. u. − 478 B. t. u. = 66 B. t. u. per pound

This heat comes from combustion of volatile gases which are distilled from the coke. Our tests show 0.5 to 1.0 per cent loss in volatile gases of coke in passing through the container, the combustion of which will account for nearly double this amount of heat.

Cost of Maintenance

The question of maintenance cost is one in which all operators are interested. In the previous articles, the maintenance was estimated at $0.04 per ton. However, over the 2-year period of operation it has amounted to $0.058 per ton of coke as follows:

Boiler repairs	$0.018
Hoist and other repairs	0.040
Total	0.058
Estimated credit due to saving on coke-car and wet-quenching equipment maintenance	0.02
Estimated net maintenance cost	$0.038

We expect that this figure will be materially decreased in the future, as it includes the cost of a large number of major changes which have been necessary to correct faulty design. Most of the difficulty has been with the skip hoist. Several changes have been made in the hoist and it is expected that its maintenance cost will be materially reduced in the future. The maintenance on the boilers has been very small. There has been no wear on the tubes and they look as good as new after 2 years' service. There has been some, though not serious, wear on the fan casings and impellers due to the abrasive dust in the circulating gases. This wear may be reduced by a change in design of the dust traps. The container brickwork is in excellent condition and should last for years. It is believed that the future maintenance could be reduced to $0.04 per ton by redesigning the hoist. However, the changes which have already been made in the hoist construction should decrease the maintenance at least $0.01 per ton. As will be discussed later, coke-car and quenching equipment maintenance has been reduced to an insignificant item. Although there are as yet no reliable data as to the extent of this saving, it seems reasonable to predict that it will amount to at least $0.02 per ton of coke. As this saving is due to the dry-quenching process, it should be credited to the dry quencher. If the credit is applied to dry-quencher maintenance, the maintenance cost of a well-designed dry quencher should not be over $0.02 per ton in excess of wet-quencher equipment and coke-car maintenance.

Investment Cost

The greatest cost of the dry-quenching system has been the investment cost. However, a recent test run at Rochester indicates that this cost may be cut in half. The quencher, the first to be built in United States, was designed with a good factor of safety, but it was not known until recently just how large this factor was. As a result of the test it has been found that the two Rochester units, which were designed for 212 tons each, are capable of handling 525 tons each with no changes whatever. Running at this capacity reduces the steam production to 475 pounds per thousand pounds of coke and increases the temperature of the outlet coke from 550° F. to 700° F., which can be easily handled. The quencher was actually operated under these conditions during the test; that is, the entire coke production of 525 tons per day was cooled in one container with the results as noted above. Inasmuch as it was impossible to increase the gas circulation rate above 21,000 cubic feet per minute with the present equipment it was impossible to prove by test that the steam production of 506 pounds per thousand could be maintained with increased gas circulation. However, considerable data were obtained by noting temperature conditions at various rates of circulation under 21,000 cubic feet per minute and curves were plotted which when extrapolated indicated that the present steam production may be economically maintained at the faster rate of quencher operation. By increasing the circulation rate to approximately 35,000 cubic feet per minute, which requires an additional investment of $10,000, the same steam production of 506 pounds per thousand could be maintained. It is impossible at this time to state what the ultimate capacity of the dry quencher is and what the limiting factors are.

Thus we see the greatest objection to the dry-quenching process—namely, high investment cost—has been eliminated, and the process becomes a very attractive one from the economic standpoint as well as others which will be mentioned later.

Effect on Quality of Coke

The effect of dry quenching on coke quality is very important to producers of both domestic and industrial coke. The question of size is probably the most important to operators producing industrial coke, although the objections to small sizes are rapidly becoming less weighty. The quencher as installed at Rochester produces smaller average sizes of coke than the wet-quenching process but it produces a coke of stronger characteristics and more resistant to further handling. However, it is just as certain that the breakage to a very large extent is unnecessary and with proper design of the equipment it could be reduced greatly. For producers of domestic coke breakage is desirable. Tests made at Rochester show that sizes of the wet-quenched coke after crushing are very similar to the sizes of the dry-quenched coke and that there is no increase in breeze as a result of dry quenching. The subject has been thoroughly covered in the previous papers and recently further tests have been run which verify the original data.

Cleanliness of Coke

Of greatest importance in the production of domestic coke is cleanliness of the coke. The dry-quenched coke is undoubtedly much cleaner than wet-quenched coke, for the reason that a large part of the very fine dust which adheres to wet-quenched coke is removed in the dry quencher and the coke is conveyed to the storage bins free from most of the dust which is always seen clinging to the wet-quenched coke. A large part of the dust discharged with the coke from the quencher is removed by the producer fuel screens. Of course, there is a small amount of very fine dust left in the coke and, if the coke is delivered to the customer dry, it is objectionable. To remove this objection all coke is sprayed with water at the storage bins after screening for the fines.

Efficiency of Burning

Another point of very great importance to industrial users of coke, such as water-gas, producer, and blast-furnace operators, is the fact that dry-quenched coke is more efficiently burned than wet-quenched coke, the theory being that in wet quenching water is drawn into the heart of the coke. When this coke is used in a water gas machine or producer, the surface moisture only is driven off the coke at the top of the fuel bed. The moisture in the heart of the coke is not driven off until the coke reaches the reaction zone. The temperature of the reaction zone is thereby lowered, which reduces the steam decomposition, thus affecting the efficiency. Although some operators may question the theory, the fact remains that there is an actual fuel saving in using dry-quenched rather than wet-quenched coke. At Rochester we have had a very good opportunity to prove this point in our producer operation, as we have been able to operate on both kinds of coke. The following data were obtained over a three-week period for dry-quenched coke operation and two weeks for wet-quenched coke operation:

	Dry-Quenched Fuel		Wet-Quenched Fuel
Moisture in fuel which consists of two-thirds breeze, per cent	6.4		11.4
Fuel used per ton coal carbonized, pounds dry	245.8		252.1
Difference between wet and dry fuel, pounds		+6.3	
Ash content of producer fuel	17.8		15.9
Carbon per ton coal carbonized, pounds	202.0		211.9
Difference between wet and dry carbon, pounds per ton		+9.9	
Theoretical fuel required to evaporate excess moisture in wet producer fuel, per cent			0.6
Theoretical carbon required to evaporate moisture 211.9 × 0.006, pounds per ton			1.3
Total actual extra carbon required because of moisture in producer fuel, per cent			4.7

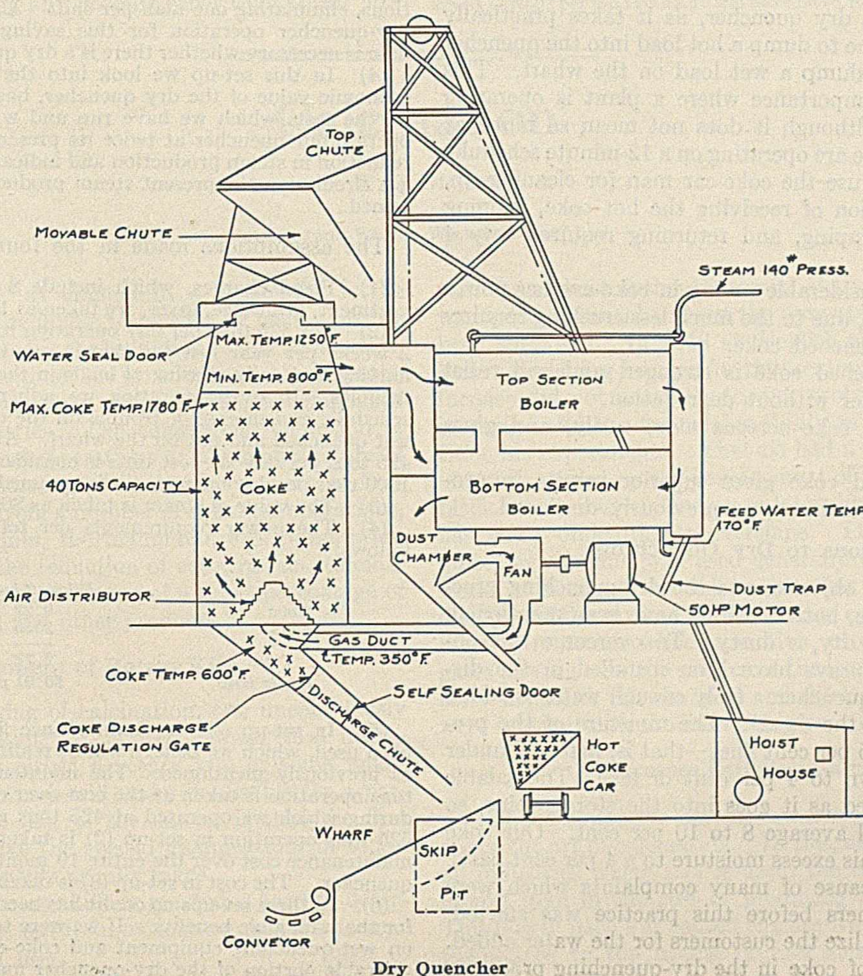
As indicated in the above tabulation, the theoretical fuel required to drive off all moisture is 1.3 pounds per ton or 0.6 per cent of the total carbon. We must therefore account for 8.6 pounds of carbon, the additional fuel required when using wet fuel, which we explain by the decreased fuel-bed temperature theory. Since this test the actual daily underfiring figure has been much lower—230 to 240 pounds of fuel per ton of coal carbonized—this with producer fuel of 3 to 4 per cent moisture.

Dry producer fuel results in a much more uniform fuel bed, making it possible to use a larger proportion of fines than is possible when using wet fuel. This is also a big advantage, as it means that more of the low-value fuel may be used, and salable coke is released for the domestic market.

It will be observed in the above table that the moisture of the dry-quenched coke is 6.4 per cent. This is high, owing to the necessity of wetting the coke during the test period, because of difficulties which were being experienced with dusty coke at the storage bins. These difficulties have now been remedied, and the producer fuel moisture is held below 4 per cent. This moisture is, of course, surface moisture, as it is applied in the discharge chute to reduce the dust condition after the coke has been cooled to 600° F. in the dry quencher, and therefore if our theory is correct it should not affect the fuel bed temperature as much as wet-quenched coke of the same moisture content.

Intangible Benefits of Dry Quenching

(1) Coke-car maintenance has been reduced to almost nothing. Dur-



Dry Quencher

ing the two years of dry-quencher operation there have been no major repairs to the quenching cars. Practically all maintenance has been confined to brakes, air compressors, and motors. The steel work shows no signs of corrosion, and with the exception of some cracked plates the cars look as good as new.

(2) There has been no maintenance on quenching apparatus. Of course, the quenching equipment has been used only occasionally, and could be much smaller, which would reduce capital expenditure.

(3) With wet quenching, winter operation of conveyor belts was always attendant with serious difficulties, such as frozen belts, ice building up on pulleys, belts pulling apart on starting owing to frozen idlers and pulleys, increased power cost due to slipping, and greater resistance offered by stiff belts. With dry-quencher operation all these difficulties have been avoided. The coke, being warm and dry, eliminates all ice troubles, and should result in longer life of belts. With wet-quencher operation it was always necessary during severe weather to have at least one extra man per shift on belt operation. Last winter, with dry-quencher operation, no extra help was necessary and maintenance was no greater than in the summer.

(4) Ice formation on coke-car tracks after the wet quencher and on the wharf is eliminated with dry quenching.

(5) As has been pointed out previously, there is a reduction of approximately 0.5 to 1 per cent volatile matter in the coke in the dry quencher. Carbonization of green ends and tops is completed in the quencher, and the possibility of "green" coke reaching customers is reduced to a minimum.

(6) There is an appreciable saving of coke-car operators' time. The wet-quenching operation requires about $1^1/_2$ minutes at least with 2 to 3 minutes for draining. All this time is saved with a dry quencher, as it takes practically the same length of time to dump a hot load into the quencher bucket as it does to dump a wet load on the wharf. This is an item of great importance where a plant is operating on a fast schedule, although it does not mean so much at present to us, where we are operating on a 12-minute schedule. It does permit us to use the coke-car man for cleaning up, as his regular operation of receiving the hot coke, running to the quencher, dumping, and returning requires only 4 minutes.

(7) There is a considerable saving in coke-crusher power cost and maintenance, due to the much less crushing requirements of the dry-quenched coke.

(8) The dry-quenched coke is stronger, and will resist further handling better without degradation.

(9) Dry-quenched coke screens more easily, and gives a cleaner product.

(10) Dry-quenched coke gives superior results in producer or water gas machines, as previously discussed.

Objections to Dry Quenching

To summarize the objections to the dry-quenching process, there are only two, both of which have been mentioned.

(1) The coke, being dry, is dusty. To overcome this objectionable feature, sprays have been installed in the discharge chutes of the quencher. Only enough water is added at this point to "lay the dust." The moisture of the producer fuel, which is 65 per cent fines—that is, material under $^3/_8$ inch—is kept down to 4 per cent or less. The salable coke is further sprayed as it goes into the storage bins, so that the moisture will average 8 to 10 per cent. Our coke sold is corrected for this excess moisture to a 4 per cent basis. This eliminates the cause of many complaints which were received from customers before this practice was started, and yet does not penalize the customers for the water added.

(2) The breakage of coke in the dry-quenching process is due to the method of charging and discharging the quencher and, if important, could easily be prevented by proper design. The resultant coke, however, is stronger and will resist further handling better.

Breakage is an advantage to us with our domestic market, since it reduces our crushing charges and yet does not increase our breeze production.

Economic Development of Process at Rochester

Of course, the greatest advantage of dry quenching is its economic advantage. It is very interesting to follow through the development of this advantage at Rochester since the installation of the process, and to look into the future possibilities. To do this four economic set-ups have been arranged:

(1) One showing the earnings of the process operating on the basis of the original contract.

(2) One showing the earnings of the process as it is now operating after making some minor changes to improve the efficiency.

(3) One showing the earnings of the process operating on the same throughput of coke, but using new maintenance and labor figures which we expect will prevail in the future. The maintenance during the first 2 years is much higher than we feel is necessary in the future, for the reason that included in the figure is the cost of a large amount of experimental work and changes in design. These changes are expected to reduce maintenace costs materially. The operating labor will be cut in half shortly. At present it is necessary to have, in addition to the dry-quencher boiler tender, an operator to handle the discharge of the coke from the containers and the control of the hoist bucket as well as a wharf operator. All these operators have a large amount of free time. Changes are now being made, so that it will be possible to feed coke off the wharf from the dry-quencher operator's platform. As soon as these changes are completed, the dry-quencher operator will handle both his own and the wharf operations, eliminating one man per shift. Credit has been given the dry-quencher operation for this saving, inasmuch as a wharf man is necessary whether there is a dry quencher or not.

(4) In this set-up we look into the future and predict the economic value of the dry quencher, basing our capacity figures on the tests which we have run and which prove that we can operate our quencher at twice its present capacity with a small reduction in steam production and indicate that by increasing the gas circulation the present steam production rate may be maintained.

The assumptions made in the four set-ups are:

(1) Fixed charges, which include 8 per cent on money investment, insurance, taxes, are taken as 16 per cent.

(2) For 525 tons per day operation it is assumed there will be 2 weeks per year lost for shutdowns, including time for overhauling and daily missing of loads in the quencher due to minor troubles. In oven operation we adhere closely to a pushing schedule, and in case of trouble on the dry quencher the load is wet quenched and put on the wharf. At slow operating rates of 425 tons per day the lost time is considered as 2 weeks, while for 1000 tons per day operation it is assumed as 3 weeks.

(3) The value of steam is taken as $0.50 per thousand.

(4) The power requirements per ton of coke have been as follows:

	Kilowatt-hours
Hoist	0.22
Fans	2.55
Total	2.77
Power cost	$0.01 per kilowatt-hour

(5) In set-up (4) the maintenance figure $0.05 per ton has been used, which we believe will be realized due to changes made as previously mentioned. The maintenance cost used for 425 tons operation is taken as the cost over our 6 months' test period during which we operated at 425 tons rate. The cost used for 525 tons operation in set-up (2) is taken as $0.058 per ton, the maintenance cost over the entire 19 months' operating life of the quencher. The cost in set-up (3) is taken as $0.05 per ton.

(6) In these set-ups no credit has been given the dry quencher for the intangible benefits. If we were to take credit for savings on wet-quenching equipment and coke-car maintenance, a considerable portion of the dry-quencher maintenance cost, at least

$0.02 per ton, would be canceled. The saving on crushing equipment is also considerable.

(7) The steam production figure for the 6 months' test period averaged 431 pounds per thousand pounds of coke quenched. The steam production at present averages 506 pounds per thousand. These figures are for boiler conditions of 140 pounds pressure and 170° F. feed water.

(8) Labor cost is taken as $0.7292 per hour, which is the lowest rate paid for shift work in our plant.

(9) In all items but fixed charges allowance has been made for the idle periods. Fixed charges must be paid whether the equipment is in operation or not, and are so considered in these set-ups.

Conclusions

1—The dry quencher makes smaller coke, which to producers of domestic coke is a distinct advantage because of the saving of crushing costs. The dry-quenched coke, however, is stronger and will resist further handling. To producers of blast furnace or foundry coke, this may be an objection.

2—What little dust is left in the coke is very light, making it necessary to spray the coke upon entering the domestic distribution bins.

3—Dry-quenched coke is cleaner from the standpoint of fines and volatile, and is stronger to resist further handling.

4—There are many intangible benefits from the dry quenching, such as improved condition of surrounding steel work, less coke-car and conveyor-belt maintenance, saving of coke-car operator's time, and saving of crusher costs.

5—Dry quenching results in an appreciable saving of producer gas and water gas fuel, due to increased fuel-bed efficiency with dry fuel.

6—From the tabulation it may be seen that, although the dry quencher is a very attractive economic proposition at present, showing a return of over 20 per cent on the investment without considering any benefits other than steam production, it will become more attractive as the coke production is increased. We may increase the dry-quencher capacity to at least 1000 tons per day with an increase in capital expenditure of only $10,000.00. The earnings will then become some 50 per cent on the investment.

	SET-UP 1 425 tons per day 6 months' test	SET-UP 2 525 tons per day present operating results	SET-UP 3 525 tons per day new maintenance and labor figures	SET-UP 4 1000 tons per day new maintenance and labor figures
Investment cost per day	$96.40	$96.40	$98.50	$103.01
Labor cost per day:				
Operator	16.80	16.80		
Boiler tender	16.80	16.80	16.80	16.45
Power cost per day	11.42	13.96	13.96	26.04[a]
Repairs per day	27.65[b]	31.06[b]	25.20[c]	47.00[c]
Total operating cost per day	169.07	175.02	154.46	192.50
Total pounds steam produced per day	366,350	531,300	531,300	1,012,000
Net steam produced per day. Deduction loss due to shutdowns	351,696	510,048	510,048	951,280
Value of steam at $0.50 per M	$175.84	$255.02	$255.02	$475.64
Total operation cost per day	$169.07	$175.02	$154.46	$192.50
Saving per day	$6.77	$80.00	$100.56	$283.14
Saving per year	$2471.05	$29,200.00	$36,704.40	$103,461.10
8% money invested per year	$17,600.00	$17,600.00	$18,000.00	$18,800.00
Total earnings	$20,671.05	$46,800.00	$54,704.40	$122,261.10
Earnings on investment, per cent	9.1	21.2	24.3	52.0
Cost of steam per M pounds	$0.4807	$0.3431	$0.303	$0.202

[a] For a new installation undoubtedly changes in the boiler, gas ducts, and coke container design would reduce resistance to gas flow and therefore reduce power cost.

[b] In these maintenance costs no credit has been allowed for savings on coke-car and wet-quenching maintenance due to dry quenching, which we estimate at $0.02 per ton of coke. If this credit is allowed, the dry-quencher maintenance will be reduced approximately 34 per cent.

[c] As in set-ups 1 and 2, no allowance has been made in this figure for savings on coke-car and wet-quenching maintenance. If we make the same credit of $0.02 per ton this figure will be reduced 40 per cent.

Calcination[1]

W. S. Dickie

Vulcan Iron Works, Wilkes-Barre, Pa.

"CALCINATION," as defined in a dictionary, is the act or process of reducing to powder by heat; thus the calcination of lime is the reduction of limestone, shell, or chalk to lime. This confines the art to rather narrow limits, as is proved by a short summary of things being accomplished today in various industries. The commercial definition of the word will include such operations as the manufacture of Portland cement, the burning of lime, the recovery of lime from sludge emanating from a number of chemical operations, the manufacture of paints, the manufacture of refractories, the making of plaster, the reduction of coke, in fact, calcination has its part in the manufacture of a great percentage of chemical, metallurgical, and other products.

Development of Rotary Kiln

Probably when thinking of calcination, one unconsciously has in mind a rotary kiln. It is well known that nearly all calcining is done in either a rotary kiln or some modification of such a kiln which will make it suitable for a particular operation. The fact of the matter is that the first rotary kiln was more like the special modifications of today than the form which the kiln usually takes.

Where the idea of a rotary kiln originated is hard to determine with any accuracy, but from various sources of information the earliest authentic record of the use of a rotary kiln was in the chemical and not the cement industry as may have been supposed. In 1848 an English engineer invented and built a revolving furnace for the treatment of black ash. His furnace did not prove successful, probably owing to defects in design and the financial inability of the inventor to continue his experiments. That he had a fundamentally sound idea was proved by the development of a successful revolving black-ash furnace a few years later, although its developers had many difficulties to overcome. The "revolver" became quite popular and was used generally throughout the alkali works of England, as well as in other countries. This evidently was the earliest form of rotary cylinder used for treatment of materials while in motion, using a flame or heated gases passing over the surface of the load. However, in these early machines the charging and discharging of the cylinder were intermittent, the ends being practically closed.

Processes Utilizing Calcination

Without doubt the cement industry has done most to advance the art of calcination. In this, as well as in practically all industries where fuel is used, the cost of the fuel is the largest item in the cost of producing the finished material. This fact in itself has caused engineers and operators to apply themselves to the saving of fuel and to find means and

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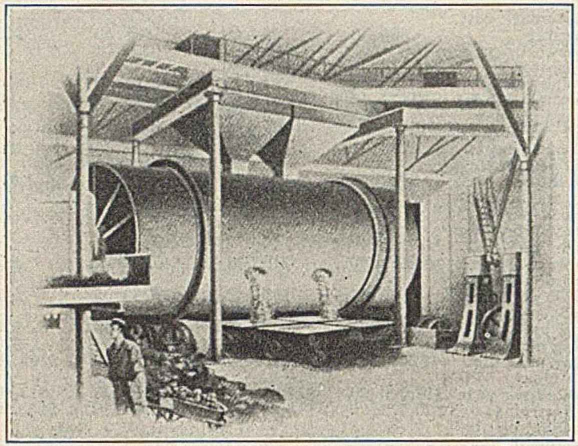
[1] Received February 27, 1929.

methods of utilizing what was formerly wasted heat. This has been accomplished by accurate control of air for combustion, the use of the best equipment, and the installation of boilers for the recovery of some of the heat which in older plants was allowed to go up the stacks. The latest development contemplates employing an arrangement of water tubes around which the calcined and finished material is passed, thus causing it to give up its heat, making steam provided the material is hot enough when passed through the equipment. In addition the treated material is cooled as well, which is desirable in most materials after calcination. If the material should not be hot enough to make steam, but it is desired to cool it, this may be done by passing cold water through the tubes continuously.



Early Type of Soda Ash Revolver

Calcining is done in processes where oxidizing is to be done, where materials are to be reduced with or without a reducing agent, where materials are made into new compounds by partial fusion, where materials are changed physically by heating, and in the reclamation of valuable materials from waste. Oxidizing is best illustrated in the burning of lime and gypsum; reducing in the treatment of barytes and lithopone; the third use, in the burning of cement; the fourth, in the sintering of iron and copper nodules; and the last, in the reburning of lime from paper-mill sludge.

The use of the rotary kiln, as stated before, in its standard or modified design, is called for in nearly all operations where calcining is to be done and naturally enough when an experiment in one industry has been successful, another industry, either kindred or dissimilar, is inclined to experiment. The closer coöperation of chemical and mechanical engineers in the working out of problems has been more marked of late years and is reflected in the solution of problems which often includes the use of calcining machinery resulting in the making of new products, the lower cost of operation, and the reclamation of materials from waste.

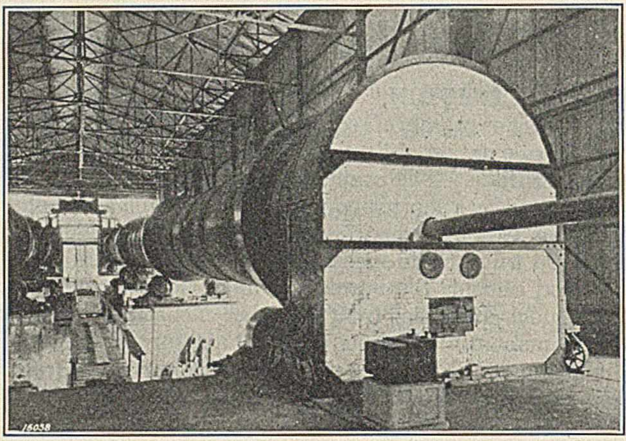
Description of Rotary Kiln

The rotary kiln, furnace, roaster, or retort is a horizontal or slightly inclined gear-driven cylinder, lined with fire brick when internally or direct fired and unlined otherwise, revolving upon two or more tires or riding rings supported on rollers, through which moves a constant or intermittent stream of material under heat treatment at various temperatures. The heat is applied by means of the flame and gases from fuel combustion coming in direct or indirect contact with the material that is traveling through the cylinder. These heated gases usually pass through the cylinder and over the load in either the opposite or same direction as the flow of material, which is known as the direct method of treatment, but they may also be applied indirectly by conducting them through a combustion or heating chamber surrounding the shell prior to their exit into the atmosphere. When the heat application is direct either an oxidizing or reducing flame may be employed, although the former is by far the more commonly used.

Use in Cement and Lime Industries

The most common type of kiln is that used in the cement industry. It is a cylinder varying in diameter from 2 to 15 feet and in length from 20 to 350 feet, usually lined with fire brick or some other refractory material to protect the shell from the high temperatures which are ordinarily employed. The cylinder is inclined from the horizontal at a pitch of from $^1/_4$ to $^3/_4$ inch per foot; is supported by means of tires or riding rings, which are in turn supported on roller bearings; and is revolved by a train of gears, the last pinion of which engages with a girt gear surrounding the shell. This common type is modified for some uses by having its ends closed or nearly closed. In some cases the feeding and discharging are done intermittently through holes in the periphery of the shell and in others continuously through small openings in the end heads. These latter types are known as Bruckner roasters and at one time were used very extensively in this country for calcining and desulfurizing copper ores. They later were also generally used for the reduction of barytes.

The cement industry does much more calcining than any other one industry and probably led in development and experimentation. Following is the lime industry. Both vertical and rotary kilns are used in both industries, although the use of the vertical kiln in making cement is confined almost altogether to foreign countries. The use of the rotary kiln in lime-burning is not by any means new, but it was taken up slowly until the last few years, when some new lime plants, after weighing the advantages of both types, installed the rotary type. The development in these two industries probably prompted the chemical and metallurgical engineers to consider similar equipment for their manufacturing problems and today these industries are leading in experimenting.



Installation of Rotary Kiln in a Cement Plant

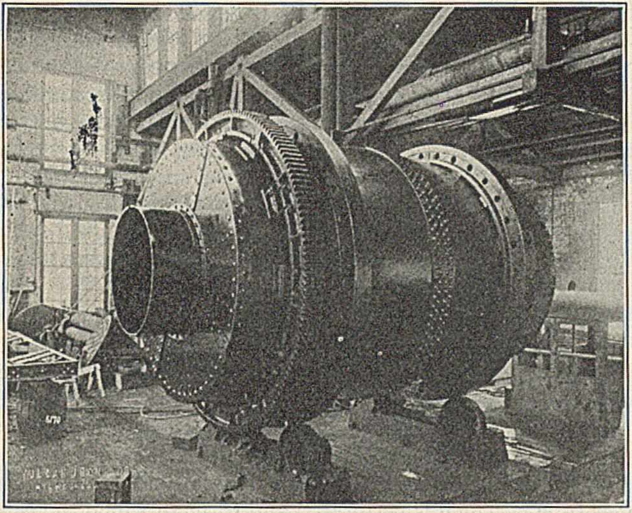
Other Applications

The earliest experiments in the use of the rotary kiln in operations other than the cement and lime industries were conducted about the year 1900. Various metallurgists were trying out the possibility of using the kiln for nodulizing blast-furnace flue dust, for desulfurizing and nodulizing the fine materials coming from the concentrating tables used in numerous operations, and for drying fine ores of iron and altering their physical condition by heat into particles or nodules of sufficient size to permit their use in blast-furnace reduction or for other purposes. Edison was one of the first experimenters, working out the possibilities of nodulizing the fine concentrates coming from magnetic separators; and as these early experiments began to show results, many companies built plants in which the rotary kiln was used for the above-mentioned purpose and it was not long before its use was extended to many other industries of a like nature.

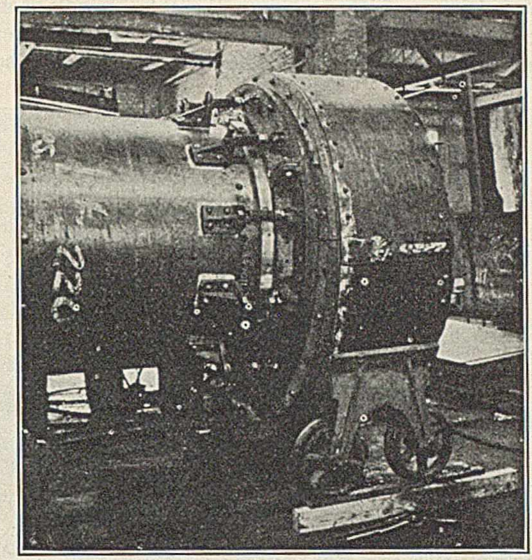
Purification of Ores—Some iron ores contain a larger percentage of sulfur than is permissible; since ore shippers are penalized proportionately for excess sulfur, it is not surprising that experiments were conducted with the idea of eliminating the excess sulfur by calcination. A number of companies installed kilns and are now desulfurizing their ores. Copper pyrites may be roasted and the sulfuric acid recovered; the residue can then be leached for the copper and the iron oxide nodulized and sold to blast furnaces, this last being taken directly from the leaching tanks to the kilns. Copper ores containing high sulfur may be successfully desulfurized and fine copper ores and smelter flue dust have been treated in a rotary kiln. The treatment of this material has been a serious question because of its fine condition when coming from the concentrating tables. It has also been proved a profitable investment to nodulize the Franklinite zinc ores, and nodules containing more than 20 per cent zinc were obtained from ore containing about 17 per cent zinc with little or no loss of metal.

Aluminum and bauxite ores are being calcined, the first experiment being conducted in 1902. In some cases the treatment of this material is more of the nature of dehydration, although kilns rather than driers are used because of the high temperatures necessary. Very likely all of the aluminum used today has been treated in a rotary kiln and perhaps the same can be said of all bauxite products.

Alteration of Barytes—In the treatment or, as it is more commonly known, the alteration of barytes calcination plays its part. In the olden days—and in fact in some plants today—the alteration of barytes to barium sulfide was accomplished in what was known as a Bruckner roaster. Barytes or barium sulfate is only soluble in acid and the practice was to crush the sulfate and mix it with from 25 to 30 per cent of ground coal or coke and calcine it in a reducing atmosphere. Because of the low temperature required, it was possible to use a hand-fired furnace, although of course all joints between furnace and roaster and roaster and gas flue had to be kept tight to prevent air leaks. With the Bruckner roaster the charging and discharging were done through manholes and, as might be supposed, the operation was of necessity slow. In this industry marked progress in calcination is shown. It is turning slowly but surely to the use of a rotary kiln for the alteration, thus gaining what was first thought to be the advantage of continuous operation, but what has proved also to be the more economical operation. For not only was there the saving in time which resulted from the continuous operation, but there was also the reduction in labor and in carbon added to the crushed barytes as well as a considerable saving in the fired fuel. The first experiments in this operation were conducted about 1914 and a great many difficulties had to be surmounted. The best proof of the success of the first experiment is the fact that the company that made it installed a second rotary kiln a few years ago.



Old-Style Bruckner Roaster

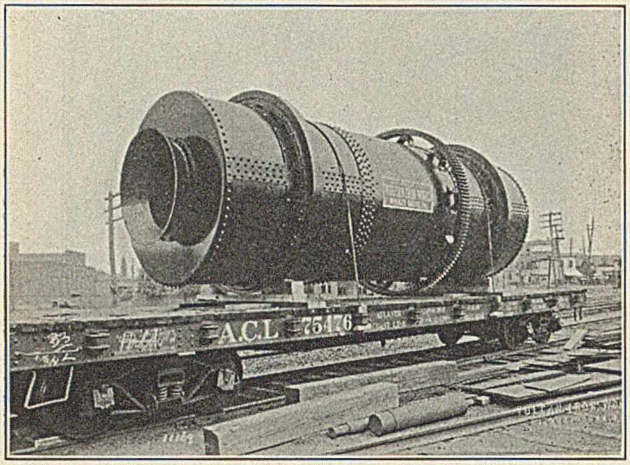


Sealing Device for a Lithopone Kiln

Calcination of Lithopone—It was a short step from the alteration of barytes to the calcination of lithopone, principally because lithopone is part barium sulfide and the users of rotary kilns on barytes were naturally the first to try calcining lithopone. Again we have a reducing problem and one even a little more difficult, because any excess air leaking into the kiln discolors the lithopone and makes it useless. This difficulty was overcome by the use of sealing devices at both ends of the kiln shell to make them absolutely air-tight. Several other paint products bearing a close relationship to lithopone are calcined in rotary kilns, the products being known by trade names and the operations being more or less secret.

Use in Sugar-Refining—In two of the leading sugar refineries in the country calcination has taken the form of revivification, where material used in refining the sugar is used, revivified, and re-used, with a small addition of virgin material from time to time. In one plant the bone black, after it has gathered up organic matter in its part in the refining of sugar, is sent to the rotary kiln where the organic matter is burned out. Eventually the bone black must be discarded but, as can be seen, a considerable saving is effected. This installation is unique also in that part of the fuel gases are returned to the firing end of the kiln to make doubly sure of a reducing atmosphere. In the other plant a foreign process is being employed in the making of sugar from beets, which includes the use of barium silicate. The user alters his barytes in a small kiln and revivifies the barium silicate in larger kilns. Again it is necessary to have a reducing atmosphere and organic material is burned out. The treatment in the kilns also brings about the return of the barium silicate to its original physical state which had been changed in its use in the sugar mill.

RECOVERING MATERIALS IN PAPER MILLS AND ELSEWHERE—Every year additional kilns or revolvers are put in paper mills, the former being used in reburning lime from sludge and the latter for the recovery of alkali from waste liquor. In lime-reburning the sludge originating in the manufacture of paper by the sulfate process is filtered on a mechanical, continuous filter, generally of the rotary type, and the filter cake is fed into the upper end of the kiln. The operations in the kiln consist of driving off the water in the cake, burning off the organic matter which has been gathered in the treatment of the wood pulp, and finally calcining the remaining solids. A small loss of lime is noted in each cycle, but the deficiency is made up in new lime. The reburning of lime in this application of calcining overcame a difficulty that paper manufacturers had previously encountered—namely, the disposal of the sludge—and at the same time effected considerable saving in the amount of fresh lime required. A modified type of kiln is used in paper mills employing either the soda or sulfate process for recovering the alkali or black ash from waste or black liquor. After the liquor is concentrated, it is fed into the revolver at one end and leaves the other, an ash. The concentrated liquor will support its own combustion and therefore movable fireboxes are used, being set on a traverse track in front of the various revolvers to start combustion and also to maintain it at times. A decided saving in operating costs in paper mills is effected by these two calcining operations.


Shell for a Soda Ash Rotary

While the paper mills are the greatest users of lime-reburning equipment, there are other places where it would be a money saver. In practically all cases the lime sludge is a waste product from an operation which calls for the use of lime as a causticizer. Among these there is lime used in the manufacture of soap, in the treatment of sewage, in the making of magnesia insulating products, and in the manufacture of rayon. Not always is lime recovered or even recoverable, but the possibility should never be overlooked.

CALCINATION OF GYPSUM—As is well known, until a few years ago all gypsum was calcined in stationary kettles. These kettles were in effect vertical cylinders in which the crushed gypsum was placed and usually mechanically agitated or stirred. The kettles were heated by means of a furnace, the heat being applied both at the bottom and through tubes or flues running through the rock. The bottoms of the kettles were a source of continual trouble, calling for frequent replacements due to the fact that the heat necessary for calcination had to be passed through them. This, of course, was a batch process and calcination by batches does not prove profitable if there is any possibility of making it a continuous process.

The first experiment in calcination of gypsum in a rotary kiln gave the operators the usual amount of trouble. Because of the low temperature required and the fact that temperature control was desirable, if not imperative, it looked as though more could be accomplished with a combustion chamber which approximated an ordinary Dutch oven furnace rather than a firing hood, except that special means were taken to keep any of the fuel or ashes from getting into the product. Subsequent work with the kiln, as well as the experiments of other gypsum companies, proved that the ordinary, or a slight modification of the ordinary, firing hood would give better results and without high first cost or upkeep charges. It is probable that most of the gypsum calcined today is produced in rotary kilns and, further, that future installations of calcining machinery will be rotary kilns rather than kettles. In addition to the advantage of continuous operation gained by the use of rotary kilns, there is a better product produced at a lower cost because of the reduced cost of fuel and labor. It appears that these advantages have been gained without losing temperature control, or uniform mixing or heating of the material, which were previously claimed as advantages for the kettle.

DEHYDRATION OF FULLER'S EARTH—In the dehydration of fresh or "green" fuller's earth, it is treated in a rotary kiln, the free moisture being removed and in some cases the water of combination also eliminated. The earth is used as a decolorizing agent in the filtration of oil and after having been used a number of times becomes clogged with the tarry coloring matter of the oil. It may then be revivified by reburning in a rotary kiln—in fact, by the same one which first treated it. Temperature control is necessary, as overburning ruins the fuller's earth for further use. The material has the unique quality of increasing in weight with each reburning up to the sixth, after which it is discarded. However, it is plainly seen that calcination, or in this particular instance revivification, is a matter of much economy in the production of oils.

INDIRECT CALCINATION IN ALKALI INDUSTRY—As was mentioned in the beginning of this article, calcination may also be accomplished indirectly by passing the heat through some other material before it reaches that being treated. In the alkali industry the rotary cylinders used are of very heavy construction, as rather high temperatures are required and the heat must be passed through the steel plate shell of the cylinder in order to treat the material, as the direct application of the flame would be detrimental to the product.

OTHER APPLICATIONS—A number of firms in other industries are calcining their product either as the complete treatment for the material or as one of the steps in its manufacture, where the process, or at least the calcining part of it, is secret. Among these are some operations for which it would take a stretch of imagination to call them calcination—to wit, the detinning of ordinary tin cans in a double-shell cylinder, the inner tube of which is perforated and through which the cans are passed. An intense flame is passed over the load and the solder and tin are melted off and pass through the perforations to the outer shell, running down to the discharge end and out. Other secret processes include what is truly calcination, such as the preparation of clay for certain kinds of fire brick, the coloring of certain shales for roofing, the treatment of cinnabar ore to recover mercury, the continuous production of coke from bituminous coal and from the heavy crude oils, the recovery of gold, silver, and other metals from ores, and many others. There is no doubt as to the progress made and no more doubt as to the future application of this, one of the oldest of arts.

The Conversion of Batch into Continuous Processes[1]

John Van Nostrand Dorr

The Dorr Company, Inc., 247 Park Place, New York, N. Y.

FROM the earliest days the basic idea behind the work of the Dorr Company has been the conversion of intermittent batch methods into continuous automatic operation. Twenty-five years ago the resistance to the introduction of continuous methods was more widespread than it is today, for engineers of the early nineteen hundreds were inclined to ridicule the suggestion that any mechanically operated continuous device could replace an apparatus having no moving parts which accomplished the same purpose. The metallurgical industry went through a meta-change during the first decade of the century from batch to continuous methods, and heavy chemical manufacture has seen a similar, though not as yet so extensive, change more recently. History has shown, however, that the change from intermittent to continuous methods in a given industry is inevitable once the machines have been developed and the technical men shown the far-reaching beneficial effect of continuous processing.

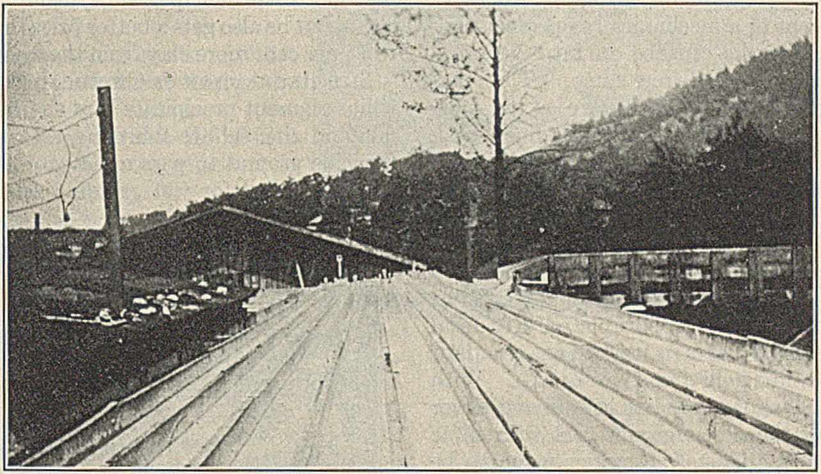
Today, while there is still room for improvement, whatever skepticism used to exist regarding machines and continuous operation has been largely removed. It has been shown that not only do machines perform the same work as that performed by the best and most skillful operators, but they actually do better work with virtually no attention, since the results are uniform from day to day and are little affected by the diligence or negligence of the operators. The mechanically operated industrial process, far from being one which requires a skilled mechanic to operate it, as its critics used to contend, has now become practically automatic and foolproof.

The work of this company may be said to deal with three principal unit operations, or unit processes as they are frequently called:

(1) The separation of a portion of the solids from the remainder and the bulk of the liquid—i. e., gravity classification or selective settling.

(2) The separation of all the solids from the largest portion of the liquid—i. e., sedimentation and filtration.

(3) Mixing or keeping in suspension all of the solids in a mixture of solids and liquid—i. e., agitation.



Old-Type Clay Classifying Trough Periodically Cleaned by Hand

A few generalizations may possibly amplify the preceding statements regarding these operations. In the first place, this work tends to make all processes continuous, and sometimes self-regulating, with obvious advantages. Secondly, with few exceptions the equipment operates slowly so that the actual power consumed is small. Finally, the work has shown that when conducting any unit operation on a fine solid-liquid mixture, it is profitable to conduct it, where possible, with mechanical means, thus giving a positive action which avoids the delicate adjustments and the necessity of close attention to meet each change in conditions.

Interrelation of Industries through Common Unit Processes

Experience has shown that few industries are so specialized and sufficient unto themselves that they cannot profit from machines, methods, or ideas developed in others. We hear less today "that idea may be all right for the manufacture of ———, but our business is so different that it would never work in our plant." Having seen an idea, originated in gold and silver metallurgy, adopted universally in the recovery of all the common metals, not only hold in all groups of metallurgy but actually spread through the broad range of chemical engineering, and establish itself firmly in such unrelated fields as sugar, pigments, and sewage disposal, we feel that there is no limit to the influence that may be exerted by a new idea, device, or process in generally modifying industrial technic.

The possibilities with present-day equipment for replacing batch processes with continuous ones are practically unlimited. It will be seen that the three basic unit processes mentioned above have proved to be virtually universal ones in industrial process work, and that improvements made in them in a given industry have had a far-reaching effect in replacing batch processes with continuous ones in other industries which might at first be considered totally different from that in which the idea was first demonstrated.

Separation of a Portion of Solids from Remainder

This unit operation has always been an important one in hydrometallurgy, in which industry mechanical devices were first introduced for placing this important operation on a continuous self-regulating basis. There is today scarcely an industry of any consequence, employing wet methods and having a problem of this character, which has not profited from the use of continuous processing for the step.

Metallurgy—In the early days of the cyanide process for the metallurgy of gold and silver, a rough separation of the wet crushed ore was desired in order that the coarse sand constituent might be treated by percolation and the fine slime constituent by decantation. Separation of the slime from the sand was effected by allowing the crushed ore, suspended in water, to flow through a crude wood box with a trap door in the bottom. The slowly settling slimes passed out of the

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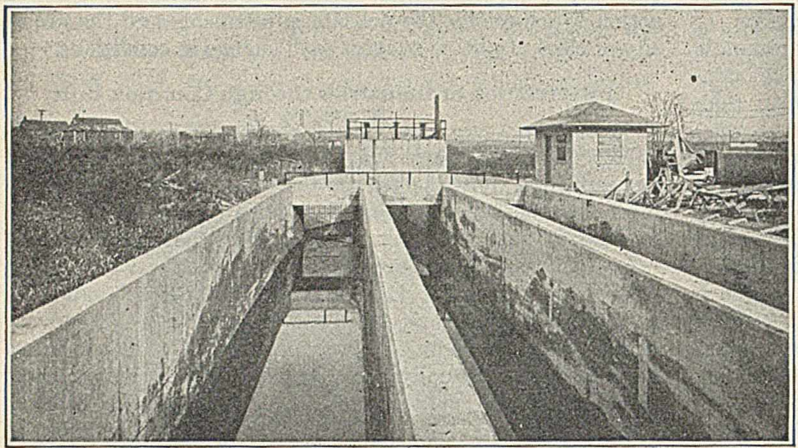
[1] Received March 5, 1929.

box suspended in the water overflow, while the quickly settling sands segregated out upon the tank bottom. The slimes were eventually collected in batch settling tanks, while the sands were dropped periodically through the trap door in the bottom of the wood box into the percolation vats below.

Cone classifiers and pointed boxes were later introduced for this work. Although they operated continuously, their separation was obtained only when certain specific operating factors, such as feed rate, dilution, etc., were carefully maintained. The spigot through which the sands were discharged was not self-regulating, tending either to choke up and cause sands to overflow with the slimes, or to discharge too rapidly causing both sands and slimes to pass out through the sand discharge.



Old-Type Grit Chambers

Reprinted from "Solving Sewage Problems," by Fuller and McClintock, published by McGraw-Hill Book Company, Inc.

Difficulties attending the profitable operation of the Lundberg, Dorr, and Wilson mill in South Dakota, because the existing equipment failed to give a slime-free, readily leachable sand, led to the development of a mechanically operated continuous device for separating the crushed ore into two products—a slime-free sand and a sand-free slime. This machine was the forerunner of what is now known as the Dorr classifier. Consisting essentially of a shallow inclined tank with an overflow weir at the lower end and a variable speed reciprocating mechanism for advancing the coarse settled material up the inclined bottom to the point of discharge, it gave a leachable sand and changed an unprofitable mining venture into a financial success.

The first engineers to see the classifier pronounced it an interesting device but considered it applicable only to local conditions. Within a very few years its use became standard practice in cyanidation in most gold and silver camps. With the introduction of the "all-slime" process in gold and silver metallurgy, wherein all of the ore is ground wet to a slime finer than 100 or 200 mesh, the Dorr classifier came to be operated in closed circuit with the grinding mill, the fine classifier overflow going to the decantation plant and the coarse rake product being returned to the mill continuously for further grinding. With the advent of the flotation process for copper, lead, zinc, and other ores and the need of grinding much finer than for gravity concentration, the Dorr classifier and the "closed-circuit" grinding system were adopted in preference to less efficient methods in the milling of virtually all the metalliferous ores.

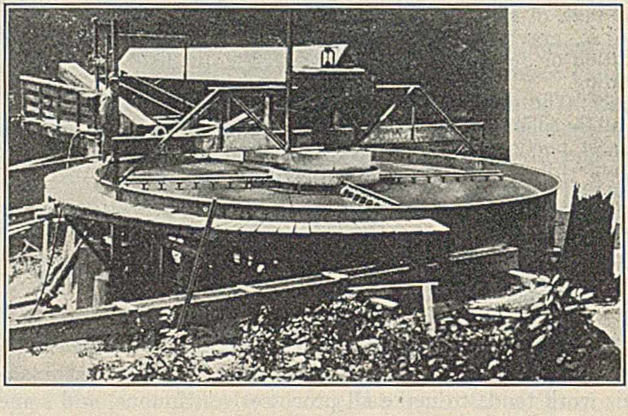
The Dorr classifier has greatly modified mill practice. From the original unit with a capacity of 50 tons per day it has been developed to a point where a single Dorr bowl classifier 20 feet wide and 42 feet long with a 28-foot diameter bowl can handle easily 3000 tons of ore per day. In the metallurgical industry the system of closed-circuit grinding made possible by the continuous mechanical classifier has on a very conservative basis reduced the unit cost of grinding 30 to 40 per cent and has reduced the consumption of steel balls and mill liners 15 to 25 per cent. The tonnage handled in this manner in the United States is approximately 100 million tons per year or 90 per cent of the total ore milled.

Pigments—Fine pigments, such as whiting, ocher, sienna, baryte, red iron oxide, and clay, are generally prepared by water-floated methods. The dilute water-pigment mixture used to be flumed through long troughs, the velocity being such that the undesirable coarse particles settled out to the exclusion of the desirable fines, which eventually passed out of the trough to settling tanks, and later to filters and driers. Periodically the troughs were taken out of service to permit laborers to shovel out the accumulated waste material, which invariably contained a large amount of valuable fine material entrained with it.

The similarity of pigment floating and ore classification is evident. In all of these pigments the Dorr bowl classifier has shown surprisingly good results, making in most cases separations from 200 to 325 mesh on a continuous automatic basis with no shutdowns for manual cleaning and with no appreciable loss of product in the sand reject.

A Virginia ocher producer abandoned 300 feet of flume and laid off two negroes whose job it was to provide agitation by shuffling back and forth all day in the flume, and put in a bowl classifier. Formerly he used to pass the water-floated ocher through a silk lawn, but he does not need that now as his bowl overflow is all through 300 mesh. A North Carolina clay producer replaced 700 feet of manually cleaned flume with a single bowl classifier and reports that not only has he laid off three men per shift, who formerly kept the flumes clean, but he also gets a better price for his clay and recovers 10 to 15 per cent more clay from the same tonnage of run of mine.

Size Regulation of Chemical Products—Lithopone, the white pigment precipitated by the interaction of barium sulfide and zinc sulfate solutions, after calcining and quenching must be ground to pass a 300- to 325-mesh screen. Former practice called for wet grinding of the quenched product in batch tube mills, periodic discharge of the milled product with a large amount of dilution water into pointed boxes, and collection of the box overflow as finished product, while the lithopone settling on the box was removed and reground with

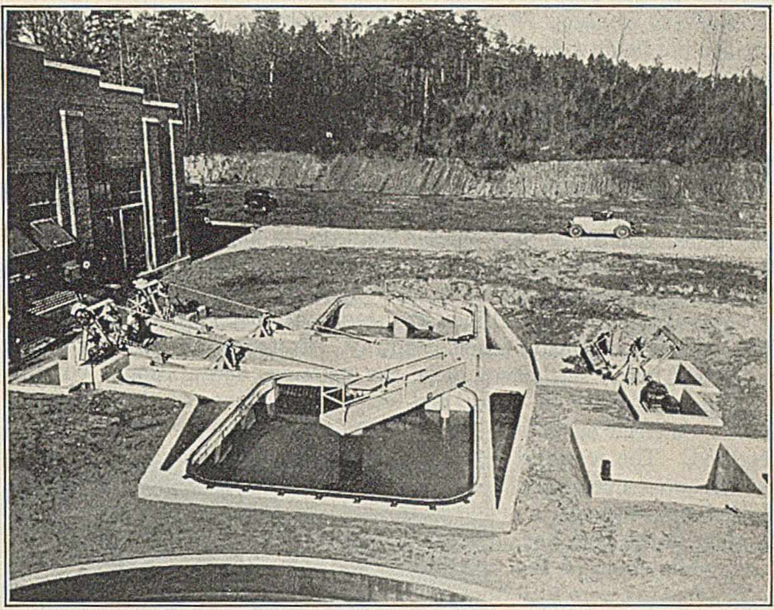


Dorr Bowl Classifier Which Replaced 700 Feet of Settling Flume, Thereby Reducing Operating Labor and Improving Product a subsequent batch. The uneconomical aspects of batch grinding in this manner are reflected in operating results at one plant studied. With 99 per cent 300-mesh finished lithopone as the goal, it was found that a 90 per cent 300-mesh product was obtained in one hour's grinding, but that eight additional hours of grinding were required to produce a 99 per cent 300-mesh product. This was a natural result of batch grinding methods in which a large percentage of the charge must be ground much finer than the desired size in order that all of it might pass a screen of this size, as well as the fact that failure to remove finished material as soon as produced prevents the balls from performing useful work on the coarse material owing to the surrounding mass of fines.

Most of the larger manufacturers of lithopone, recognizing the advantages of the grinding technic developed in the field of metallurgy, have adopted continuous grinding of lithopone with the continuous tube mills close-circuited with Dorr classifiers and Dorr hydroseparators. With a continuous feed and continuous discharge of finished lithopone, appreciable savings have been made over batch methods. The mill is fed at several times its batch capacity and the discharge contains only a small portion of sufficiently ground lithopone, for size separation is now centered at the classifier and the hydroseparator, not at the mill, and every effort is made to remove the finished product from the system as soon as formed. Savings in power costs, grinding media, and labor are considerable and conform closely to those being obtained in representative metallurgical operations.

Sewage Treatment—Sanitary engineering might at first appear to be a profession so unrelated to metallurgical engineering that neither could gain any worthwhile ideas from the other; yet experience has shown that they have much in common. Grit, sand, and other inorganic matter associated with municipal sewage have always presented difficulties at the sewage treatment plants. They lodge in pipe lines, cause excessive wear on mechanical equipment such as screens and pumps, and occupy valuable space which is needed for biological purposes.

Common practice up to a year ago was to provide a number of grit chambers in the influent channel to the treatment plant. The cross section of the chambers was such as to reduce the velocity of the incoming sewage to a point where the grit settled out to the exclusion of the organics. From time to time the grit chambers were cut out of service in sequence and the deposited material removed by hand or by grab buckets. Although these chambers did protect the equipment which followed, they were far from ideal—first, because they were expensive to clean; second, because a multiplicity of units was needed in order to maintain uniform velocity with varying flows; and third, because so much putrescible organic matter was carried down with the grit that the removed material was unsightly and highly odorous.



Two Dorr Detritors Continuously Removing and Washing Sewage Grit

Tests conducted with a Dorr bowl classifier indicated that the classifier principle was applicable to continuous grit removal and washing. Experimental work in a flume through which water was allowed to pass at different rates, and in which sand of variable sizes was fed at variable rates, established the underlying physical data on the basis of which the Dorr Detritor (automatic grit chamber) was designed. This machine utilizes the bowl classifier principle, but has a square bowl with a reciprocating rake compartment along one side in order to conform to sanitary practice and the rather special requirements of this particular problem.

In the Dorr Detritor the grit is deposited in the square collecting tank as the sewage flows across the tank at a greatly reduced velocity. The settled grit is raked outward by a special mechanism and deposited in the grit-cleaning channel, where it is given mild mechanical agitation by the classifier mechanism which releases any entrained organics. The grit is raked up the incline to the point of discharge, being first permitted to drain on the above water section of the incline.

Batch grit removal used to involve multiple units and manual labor and produced a 50 to 60 per cent moisture residue containing from 13 to 25 per cent putrescible organic matter. Continuous grit removal in a Dorr Detritor over a period of several months showed that duplicate units were not required, labor was only that of handling the grit containers, moisture content averaged 25 per cent, and putrescible organics were reduced to less than 5 per cent.

Separation of All Solids from Largest Portion of Liquid

This unit operation is one of almost universal application. There is scarcely a branch of the process industries which is not at one point or another confronted with a problem of this sort which may be handled more profitably on a continuous automatic basis than by batch methods.

Metallurgy—In the cyanide process the slimes were handled in intermittent decantation tanks equipped with spigots for the discharge of the settled slimes and siphons for decanting the supernatant clear solution. While engaged in the remodeling of the Mogul Mining Company's mill at Pluma, S. D., the writer developed the Dorr thickener for continuously dewatering the classifier overflow. This machine was adopted generally in cyanidation, and later its use became practically standard practice in other branches of metallurgy—chiefly copper, lead, zinc, etc.—where the thickener rapidly established itself for dewatering flotation concentrates, and tailings. More recently it has been used for effecting a change of solution between steps in selective flotation.

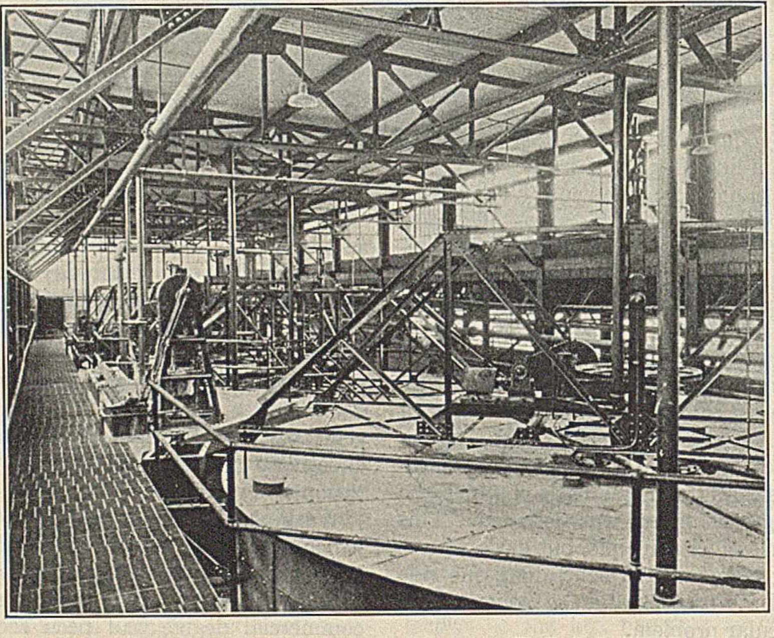
Washing the slimes after cyanidation was an operation which used to be carried out by batch settling, decantation, and repulping of the sludge, first with weak wash solution and finally with water, until a removal of pregnant solution to a commercial degree had been secured. Settling cones had been tried for carrying the work out continuously, but trouble invariably resulted from the accumulation of solids on the sides of the cone and the impossibility of securing a continuous, dense discharge.

By means of the continuous thickener continuous countercurrent decantation was made a success and resulted in changing the cyanide process from a batch process to a continuous one. A row of Dorr thickeners arranged in series on slightly different elevations constituted the "C. C. D." plants, as they later became known. The agitated slimes, suspended in gold-bearing solution, entered the first thickener, the overflow from which was sent to precipitation of gold by zinc dust or shavings, while the sludge was pumped through the remaining thickeners, being mixed after each settlement with a stream of wash solution cascading from one thickener to the other in the opposite direction. Wash water, introduced in the last thickener, flowed by gravity toward the head end of the plant, being enriched in dissolved values by coming in contact with progressively richer sludges. This enriched wash solution finally overflowed from the second thickener and, after the addition of cyanide, was used in grinding new ore. Similarily, the sludge in its passage through the various stages of decantation came in contact with progressively weaker wash solution and was accordingly impoverished in the dissolved values.

A continuous countercurrent decantation plant, consisting of five series of four thickeners, showed a great improvement over batch methods, which it replaced. The gold losses in the tailings were only 9.57 cents per ton, equivalent to an overall recovery of about 99 per cent of the values in the $8.92 per ton ore being milled.

Chemical Manufacture—With the successful demonstration of the countercurrent decantation principle in metallurgy, it became increasingly evident that the same principle was applicable to those chemical operations of a leaching, digestion, or precipitation nature in which the solution is subsequently separated from the suspended solids, either for the recovery of all of the valuable solution through washing the solids or for preparing a solid product of value free from a contaminating solution. The countercurrent principle was recognized in the chemical industry, but continuous processing had not yet made much headway. Common practice called for batch settlement after the reaction, decantation by siphon or draw-off cocks, and as many washings of the settled material as were required. The washed sludge was eventually sluiced out through an opening in the tank bottom, while some of the wash solutions were utilized for making up fresh batches or diluting the strong liquor from the first decantation.

A progressive manufacturer of phosphoric acid was the first to use a C. C. D. plant for chemical work. By installing five acid-resisting thickeners in his plant, he was enabled to produce a single strong phosphoric acid solution and continuously wash the precipitated calcium sulfate with the water which he subsequently needed for the acid digestion of his phosphate rock. Other manufacturers of phosphoric acid have adopted the method of continuous sludge washing with the result that not less than 60 per cent of the phosphoric acid produced by the acid method in the United States today is made in this manner.



Continuous Countercurrent Decantation Plant at a Kraft Pulp Mill Producing Caustic Liquor for Digesting Pulp Wood

Continuous phosphoric acid plants, utilizing not only C. C. D. but also continuous digestion in a series of three agitators, produce acid at about 75 per cent of the cost with batch methods. The following figures show wherein operating savings are secured:

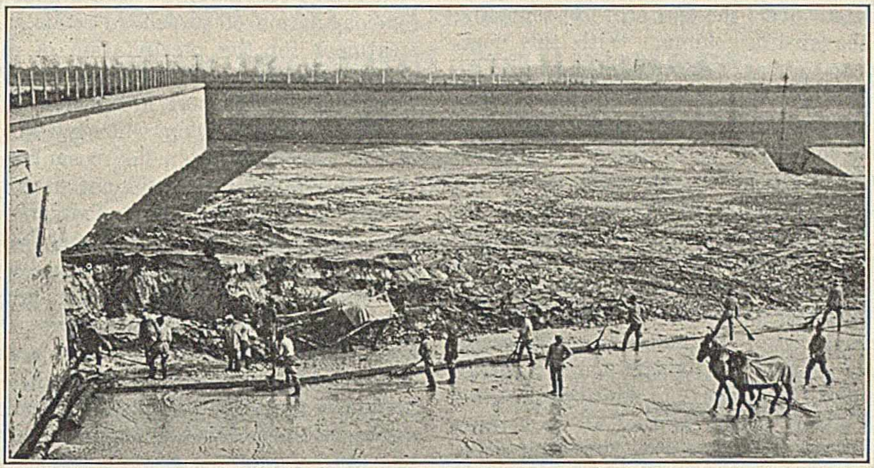
Method	Extraction P_2O_5 Per cent	Washing Efficiency Per cent	Over-All Recovery Per cent	Strength Phosphoric Acid (P_2O_5) Per cent
Continuous	97	98	95	22
Batch	94	93	87.5	17

The success of the C. C. D. system of sludge washing in the case of phosphoric acid led to its introduction in other similar chemical operations. Aluminum sulfate (alum) was handled successfully in the same manner, the pulverized bauxite after digestion with sulfuric acid yielding a fine silica residue which could be washed advantageously in the continuous thickeners which followed. In alum manufacture it was demonstrated that continuous methods not only improved extraction of aluminum oxide and washing efficiency, but also produced a more concentrated and hotter liquor (35° Bé. and 95° C.) which resulted in large savings in its subsequent evaporation to 59° Bé.

Continuous countercurrent decantation made considerable headway in the manufacture of caustic soda by the lime-soda ash process. One plant which adopted this system several years ago obtains such a thoroughly washed calcium carbonate precipitate that it has developed a market for it as whiting. Barium sulfide, used in the manufacture of lithopone and prepared by leaching reduced barytes cinder, is another chemical now made in large quantities in C. C. D. plants. In the older technic, batch leaching by percolation or intermittent decantation, there were two chief difficulties: (1) It was difficult to employ laborers owing to the depilatory qualities of the liquid and the irritating qualities of the vapors; (2) high-strength solutions were difficult to handle because of the solidification which occurred in the cooling incident to batch handling methods. About 64 per cent of the barium sulfide made in the United States is produced in countercurrent decantation plants in which the solution and solids are handled mechanically in covered and insulated thickeners, connected by insulated and closed pipe lines. The usual advantages of continuous producing are in this case enhanced by the protection afforded the laborers and the stronger and hotter solution which may be handled without danger of solidification.

The same principles have been applied successfully to the preparation of chemical precipitates, in which the solid portion of the mixture is the valuable constituent. Barium sulfate (blanc fixe), barium carbonate, titanium pigment, and lithopone are representative of those chemical precipitates which may be washed countercurrently on a continuous basis to free them from the last traces of soluble salts.

Sanitary Engineering—In probably no field were continuous settlement batch cleaning methods of separating from liquids so firmly entrenched as in sewage treatment and water purification. Up to ten or twelve years ago sedimentation was accomplished by passing the material through rectangular concrete tanks, the overflow from which was relatively clear. The accumulated solids were withdrawn periodically by hand or grab buckets or through draw-off connections in the tank bottom.



An Old-Style Water-Works Sedimentation Tank Shut Down for Manual Removal of Sediment

A modification of the Dorr thickener, the Dorr clarifier, was introduced in the sanitary engineering field and was instrumental in initiating a general acceptance there of continuous methods. The Dorr clarifier is installed in square concrete tanks with the feed entering through submerged ports along one side and the clarified effluent passing out across a weir along the opposite side. The traction mechanism arm oscillates on its central supporting column so that the corners of the tank may be effectively swept by the plow blades.

In sewage treatment the continuous collection and discharge of the solid matter prevents the septic action which sets in when raw sewage sludge is allowed to accumulate. The immediate removal of this organic matter prevents gas formation and the building up of scum and floating material on the surface. Furthermore, the entire tank volume is available for sedimentation and the removal of solids is not progressively reduced, as it used to be, by the steady accumulation of sludge.

About 5 per cent of the municipal sewage in the United States is purified wholly or in part in some type of sewage treatment plant. The most widely used treatment methods are the activated sludge process and straight sedimentation followed by sludge digestion, in both of which settling and clarification are essential steps. The Dorr sewage clarifier is used in the treatment of one billion gallons of sewage per day, which is about one-third of the sewage in the United States subjected to treatment of any sort. Among the large municipalities which have adopted continuous sedimentation are Chicago (North Side Plant), 275 million gallons per day; Milwaukee, 85 million gallons per day; Syracuse, 57 million gallons per day.

In municipal water purification, especially at midwestern cities along inland rivers, the city water supply may require special treatment for the removal of suspended solids such as clay and silt or for the removal of hardness by the precipitation of dissolved calcium or magnesium salts. In either case clarification by sedimentation is employed to remove the bulk of the solids before final treatment on filters. Large rectangular batch settling tanks used to be common at water treatment plants. Periodic shut-downs for cleaning out the accumulation and the necessity of supplying duplicate units to carry the load while tanks were out of service were considered necessary evils of water-works practice. The introduction of the continuously mechanically cleaned Dorr clarifier has greatly simplified practice and has resulted in worthwhile operating savings.

The older of the two water works at St. Louis has nine intermittent settling tanks, each 23 feet deep at the center and holding 30 million gallons. During a recent semiannual shutdown for cleaning, the first of these basins was found to contain 67,500 tons of mud, which extended to within 6 inches of the top. In the cleaning of such a basin, which is 670 feet long and 400 feet wide, men with horses and wagons entered the tank and hauled the sediment to one side, where it was flushed into a sewer leading to the Mississippi River. The cleaning of such a tank used to take several weeks.

The new water works on the Missouri River carries out the treatment on a continuous basis in four 150-foot square Dorr clarifiers. Two of these act as preliminary settlers of the raw water and two as settlers of the chemically dosed raw water overflowing the preliminary units. The settled sludge flows back into the Missouri continuously, thus making costly shutdowns for cleaning and duplicate units unnecessary.

Kansas City recently built a new water-purification plant. Four 200-foot Dorr clarifiers now continuously presettle 100 million gallons of water a day, removing therefrom 4000 tons of impurities. Beverly Hills, Calif., Edmonton, Alberta, Fostoria and Newark, Ohio, Miami, Fla., and Mamaroneck, N. Y., have adopted the same type of water-treatment equipment, but of course on a much smaller scale.

Mixing and Keeping in Suspension Finely Divided Solids in Liquids

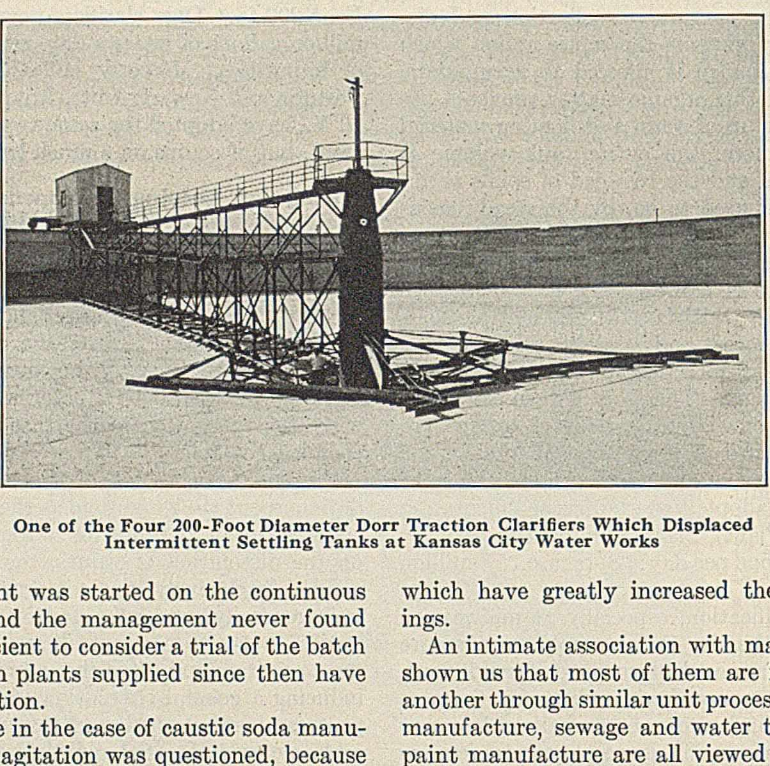
Batch mixing or agitation is probably one of the oldest unit operations known to science. It goes back beyond the earliest days of metallurgy and chemical engineering, as shown by the paintings of the ruins of Egyptian temples. It is only fairly recently, however, that continuous agitation has been developed to a point where it compares favorably with batch agitation in the case of products requiring close chemical control.

Continuous agitation of slimes was established in cyanidation about the same time as the introduction of continuous countercurrent decantation. Air having a beneficial effect on the dissolution of values, the agitators used at first depended exclusively on compressed air for mixing. The unit generally used consisted of a tall, narrow tank with a conical bottom. A central air-lift column extended from top to bottom and lifted the pulp to the top of the tank, thus inducing a general circulation of the contents. The pulp in process of agitation flowed through a series of these tanks, each one being located slightly lower than the preceding one in order to permit gravity transfer. The total cubic volume of these agitators bore such a relation to the hourly flow of pulp from the grinding system that the pulp was retained in the agitation process for the number of hours dictated by its leachability.

The Dorr agitator was developed in order to keep the coarse segregating solids more effectively in suspension by a combination of air and mechanical means and to make it possible to utilize tanks of larger diameter and more moderate height. This agitator embodied the advantage of the previously introduced Dorr thickener in that a slowly revolving mechanism moved settled solids to the center. In place of the solid shaft of the thickener there was a revolving hollow column at the tank center which served as an air lift to raise the collected segregating solids to the surface, whereupon they were evenly redistributed over the surface by revolving troughs attached to the air-lift column. With this combination of mechanical and air agitation, operation could be continued indefinitely without fear of the shutdown caused by the settlement of coarse solids, which in the past had periodically interrupted continuity of agitation. Since mechanical agitation supplemented the air, tanks could be constructed with diameters as great as 50 feet, whereas the limit with straight air agitation was from 15 to 20 feet.

The older type of batch agitation installation consisted of several separate agitators into which the materials were charged in rotation in given proportions. Agitation was maintained for a specified period of time and under precise conditions controlled by an operator, whereupon the charge was released to subsequent treatment. In continuous agitation the materials are added to the first of at least three series of connected agitators and the treated product flows from the final unit in a continuous, uniform stream. Owing to the large volume provided, frequently sufficient for a pulp detention of 24 to 72 hours, occasional analyses of the discharge from the last agitator permit corrective measures being taken at the head end of the system before the change in average pulp conditions can become serious.

Chemical Manufacture—The idea that continuous agitation of bauxite with sulfuric acid could be applied to the preparation of aluminum sulfate (alum) was at first ridiculed. It was pointed out by the critics that chemical manufacture was "a different type of business from metallurgy," and that continuous agitation could not give a uniform alum liquor with an average basicity of 0.2 per cent with a permissible variation not to exceed 0.02 per cent either way. In order to settle this point, the first continuous alum plant was arranged so that the agitators might be operated either in series for continuous agitation or in parallel for batch agitation. The plant was started on the continuous system seven years ago and the management never found the product variation sufficient to consider a trial of the batch system. All C. C. D. alum plants supplied since then have employed continuous agitation.



One of the Four 200-Foot Diameter Dorr Traction Clarifiers Which Displaced Intermittent Settling Tanks at Kansas City Water Works

The same thing held true in the case of caustic soda manufacture. Here continuous agitation was questioned, because it was believed that it lacked those means of chemical control which were considered essential in the production of a high causticity solution without the use of an excessive amount of time. The uniformly high causticities being obtained at half a dozen continuous caustic plants have shown that these objections were groundless and that excess lime need never exceed permissible limits.

In the manufacture of phosphoric acid continuous agitation has been used successfully, although it is true that several companies still employ batch methods. Experience has shown that with continuous agitation there is no difficulty in securing a complete use of the sulfuric acid and a limitation of the SO_4 radical in the phosphoric acid to an amount not exceeding 0.75 per cent.

Water Purification—Continuous dosing of turbid water for coagulation of suspended solids and continuous chemical treatment for the precipitation of dissolved salts in hard water presented special problems. The flocs formed in treatment of this sort are extremely delicate and fragile, breaking down quickly when agitated violently. A study of the time element in floc coagulation and the maximum velocity of flow which did not destroy flocs led to the development of a special type of water-treating agitator.

By supplying two or three large, series-connected concrete tanks, each fitted with a very large central-draft tube and a slowly revolving, large diameter propeller, effective water dosing is carried out continuously. Detention up to several hours may be provided in these units even when a city's entire water supply must be treated. The important design feature is the ability of the propeller to turn over these immense volumes of water, yet never permit the water velocity to exceed 1 foot per second, which is about the maximum velocity for floc retention.

General Observations on Continuous Methods

Experience has shown that there are very few industrial operations which cannot be handled more advantageously on a continuous mechanical basis than on an intermittent nonmechanical one. Recent years have witnessed general prosperity both here and abroad, a prosperity which is no doubt due largely to mass production and the use of mechanical devices which reduce greatly the labor cost per unit of product. Those who a few years ago deplored the industrial era would be surprised today to see how beneficial has been the inevitable replacement of men with machines. Not only has management benefited but also the workers, who have been relieved from manual labor in large quantities and placed in charge of machines which have greatly increased their productivity and earnings.

An intimate association with many different industries has shown us that most of them are interrelated in one way or another through similar unit processes. Metallurgy, chemical manufacture, sewage and water treatment, sugar, iron, and paint manufacture are all viewed in a new light, when it is seen that each has a similar solid-liquid separation problem which has been solved successfully in the same manner in each case. The heavy chemical manufacturer and the metal mill operator in many instances are so well versed in certain common processing methods that a fertilizer manufacturer producing phosphoric acid and superphosphate in the South would be quite at home in a gold-milling plant in Northern Canada and vice versa.

Whatever progress has been made in converting batch to continuous processes will continue in the future more rapidly as technical men in different lines of industry realize that advances made in one field may point the way to improvements in their own. The need today is for the intelligent direction of our great industrial enterprises by men who accept no method blindly because it has always been used and reject no new fundamentally sound method simply because it has never been tried out in their own particular field.

Metallic Materials of Construction for Chemical Engineering Equipment

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THE era of chemical industry is passing in which it was the general policy to build equipment of the cheapest materials available, regardless of other economic factors. The old policy once was excusable because there were so few materials really available for the fabrication of apparatus for the process industries. Today, however, the chemical engineer planning an installation is more likely to be embarrassed by the conflicting claims of a multitude of materials than by a dearth of available metallic or non-metallic supplies.

This article is intended to review in a brief manner some of the more important types of metallic materials in use at the present time, indicating in each case by a few examples their suitability for certain fields of service. The information has been largely supplied by the various manufacturers whose assistance is acknowledged at the conclusion of the article, while the writer has also drawn on the sources in the appended list of references.

Factors Influencing the Choice of a Material

Before discussing the various metals and alloys available at the present time, it may be well to note briefly the factors which should be considered in choosing a material for a specific piece of equipment. These factors may be summed up as follows:

PERMANENCE OF PROCESS—Obviously, if a process has an anticipated life of five years, it is scarcely necessary to consider an expensive material which will last twenty-five years. Technical research is moving so rapidly that obsolescence, not only of specific pieces of equipment, but of whole processes of manufacture of a given product, must be given serious consideration.

MECHANICAL PROPERTIES AND FABRICATION POSSIBILITIES—The new technology is no longer satisfied to work at low temperatures and pressures, if it can speed up reactions and increase yields by boosting either or both of these factors. Mechanical properties under high temperature are coming to rank even with corrosion resistance in importance. The availability of a material in a variety of forms and the ease with which it can be fabricated in the plant go hand in hand with its mechanical properties.

CORROSION FROM STANDPOINT OF PURITY OF PRODUCT—In general, the contamination of the product through corrosion of the material of the equipment is less important than injury to the equipment itself, but in many cases—for example, the manufacture of pharmaceuticals, fine chemicals, dyes, rayon, etc.—contamination of the product must be given great weight in the comparison of possible materials of construction.

CORROSION FROM STANDPOINT OF SERVICE LIFE OF MATERIAL—When the life of the equipment, rather than the purity of the product, is the controlling factor, an economic analysis of the over-all cost of a wide range of materials would be advisable, in case it is possible to obtain even approximate data on corrosion resistance under service conditions, or to deduce this information from careful laboratory tests under conditions approximating as nearly as possible to those of actual service. In case corrosion resistance information is available, a fair index of comparison between various materials is given by the relation:

$$\text{Comparative cost index} = \frac{\left(\begin{array}{c}\text{Initial}\\ \text{cost}\end{array}\right) + \left(\begin{array}{c}\text{Labor and shut-down}\\ \text{charges for repairs and}\\ \text{replacement}\end{array}\right) - \left(\begin{array}{c}\text{Intrinsic value}\\ \text{of scrap material}\end{array}\right)}{\text{Probable service life of material}}$$

REPLACEMENT FACILITIES—The availability of a material in a wide range of standard forms comes into consideration again here. The rapidity with which special forms may be obtained, and the possibility of repair fabrication in the plant, as by welding, are tremendously important, as they may frequently swing the decision toward a cheaper and less durable material which can be readily repaired, and away from a material which has better corrosion resistance but is expensive and difficult to fabricate or to obtain in special forms.

Given the necessary information, a fairly rational choice between materials might be made by balancing these factors against each other. Often enough it is impossible to get the fundamental information to be rational about. As a consequence many engineers refuse to take a chance on more expensive materials and stick to a steady program of repair and replacement of equipment made of our universal cheap materials—iron or steel. Although these materials have perfectly justifiable and extremely wide use in all the process industries, they will naturally be replaced in various processes by more suitable materials as the general knowledge of the possibilities of alloys increases.

IMPORTANT TYPES OF METALLIC MATERIALS

The following sections will list some of the fields of application of the various metals and alloys which are most important to the chemical engineer at the present time. Each section will include brief references to the fabricating possibilities of the materials. The composition and average tensile properties of most of the materials will be found in Table I, which has been compiled from manufacturers' statements and data in standard engineering handbooks. The values in Table I should be regarded as only approximate. Readers desiring more complete data on materials developed prior to 1924 are referred to the extensive tables published in the Proceedings of the American Society for Testing Materials for that year in connection with the symposium of this organization on corrosion-, heat-, and electrical-resistant alloys.

Iron and Steel

ARMCO IRON—Equipment to be subjected to severe chemical corrosion is not generally built of iron. Commercially pure Armco iron, containing not more than 0.16 per cent

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impurities, is, however, used in a large number of places in chemical engineering works—for example, as hoods and ducts for pickling tanks, kettles, glue cookers, beater hoods in sulfite paper plants, lids for ammonia centrifuge in tar distillation plants, crystallizers for Epsom salts, gas holders for carbon dioxide, caustic soda tanks, and as factory siding and smoke stacks. Pure iron resists the attack of dry hydrogen chloride, but must not be used for this gas where it may come in contact with any moisture. In the petroleum industry pure iron is used for oil tanks, agitators, pipe lines, weak acid towers, and other equipment.

Armco iron produces sound, homogeneous welds by either the electric or oxyacetylene processes, is excellent for cold-working, and may be hot-worked well, except in the range from 850° to 1050° C., where it is red short.

Wrought Iron—Mixed acids, below 20 per cent water, are handled satisfactorily in wrought iron, and this material is also used for caustic. Wrought iron is fabricated into equipment for anhydrous organic condensation reactions utilizing aluminum chloride, and for the production of formaldehyde. Wrought-iron piping and tubes are utilized to a large extent in the petroleum industry.

Mild Steel—Steel is used universally at present throughout the process industries for hundreds of purposes for which it is not particularly adapted from the standpoint of corrosion, but for which it is nevertheless considered to be economical, in spite of high replacement costs, because of its low initial cost as compared with more resistant materials. A few of the applications for which steel is now used would be justified even in the event of great reduction in the price of alloys. For example, concentrated mixed acids containing less than 20 per cent water are handled satisfactorily in steel, as is perfectly dry sulfur dioxide.

Steel is available in the greatest diversity of forms of any metallic material, and is readily fabricated, machined, and welded.

Cast Iron—Concentrated sulfuric acid (above 80 per cent) and caustic can be used in cast-iron equipment. Ammonia, either dry gas or liquid anhydrous, can also be handled in this material. Cast iron has been largely used in furnace parts—for example, as rake blades in Wedge and Herreshoff furnaces—but its use in this field is now being curtailed somewhat by the development of special heat-resistant alloys.

High-Silicon Iron

Duriron, containing 14.5 per cent silicon, is representative of the high-silicon irons, which are extremely valuable because they are practically unaffected by sulfuric, nitric, acetic, phosphoric, and cold hydrochloric acids, alum solutions, and many other corrosive substances. The resistance of these materials causes them to be used for acid pumps, acid-mixing nozzles for pickling tanks and oil refineries, acid-sludge-concentrating equipment, circulating steam jets, and welded coils for heating pickling tanks and chromium-plating baths, rake blades for Dorr classifiers in wet metallurgical processes, tubes for Cottrell precipitators handling acid mists, and equipment for handling rayon dope. Mixing nozzles of this same material are excellent for introducing chlorine into caustic to produce hypochlorite bleach. Another application of high-silicon iron is as anodes in the electrolytic refining of copper or of cadmium.

High-silicon iron is available only in the cast form, and is so extremely hard that it cannot be machined, but must be finished by grinding. The development of super-hard tool materials, such as Carboloy and Borium, may make possible the simple machining of Duriron castings, but success has not yet been achieved along this line. High-silicon iron may be welded with the oxyacetylene flame. The design of castings is limited by the necessity of eliminating large plane surfaces and of using heavily supported sections. Pipe and fittings, valves, cocks, fans, pumps, and jacketed and unjacketed kettles of capacities up to 650 gallons are standard items of equipment. Complete tubular heat exchangers are built up by welding from Duriron pipe.

Chrome-Iron Alloys

For convenience, the chrome-iron alloys applicable to chemical engineering problems may be classed in four groups on the basis of their chromium content:

(1) Alloys containing from 12 to 15 per cent chromium with a minimum carbon content of 0.3 to 0.4 per cent. These are the "stainless steels." The stainless properties are developed only after heat treatment, which is also necessary after hot-working to prevent brittleness. Chrome-iron alloys with the above chromium content and 1 to 2 per cent carbon are very hard and resistant to abrasion, and are put to good account in the wearing parts of crushing and grinding machinery, agitators, etc.

(2) Alloys containing from 12 to 15 per cent chromium, with low carbon content, usually under 0.12 per cent. These "stainless irons" are really mild stainless steels, since they also air-harden after hot-working, and care must be taken to properly anneal them after such work.

(3) Alloys containing 16 to 20 per cent chromium, with carbon usually below 0.10 per cent, and silicon usually present up to over 1 per cent. These have slight air-hardening tendency and may be classed as actual stainless irons. The alloys of this class have good resistance to corrosion, high ductility and workability, and good strength.

(4) Alloys containing more than 20 per cent chromium, of which the most common representatives run between 24 and 30 per cent. As the resistance to corrosion of the chromium-iron alloys increases with increase in chromium content, these alloys offset their increased cost by increased resistance to attack, such as corrosion and oxidation at high temperatures. They may be fabricated only after proper heat treatment, but are readily cast. Alloys containing chromium upward of 2 per cent together with high carbon, from 2 to 3 per cent, have great abrasion resistance.

Of the varied and important applications of chrome-iron alloys in the process industries, perhaps the most important is their use for equipment in the ammonia oxidation process for making nitric acid. Since this subject is treated in detail in another article in this issue,[2] only brief reference will be made to it here. Chrome-iron tubing is used in this process, where it must stand the combined action of pressure, temperature up to a red heat, and the attack of nitric acid gases. Nitric acid towers built from 16 to 20 per cent chromium alloys, with or without appreciable amounts of silicon, have proved eminently satisfactory, and hot, concentrated nitric acid is handled well in this same material.

Chrome irons of high chromium content have a great resistance to the attack of sulfur dioxide and other sulfur compounds, even at elevated temperatures. Rabble arms of Duraloy, or other chrome irons in the 24 to 30 per cent chromium class, installed in Herreshoff and Wedge furnaces used in copper and zinc smelting plants have shown long service lives. The same type of material is used for skid bars in billet-heating furnaces, eliminating the water-cooled construction necessary with steel or cast iron, and thereby lowering heat losses. An extremely important application of the same material is in the construction of metal recuperators for recovering the sensible heat from the waste gases of billet and forge furnaces and from glass-melting tanks, some such recuperators having been in satisfactory operation now for five years without attention.

Mixed acids used in rayon manufacture, and in cellulose work in general, have been handled in high-chromium alloys, but the results in this field have been somewhat uneven.

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[2] Mitchell, p. 442, this issue.

Table I—Selected Data on Metals and Alloys

MATERIAL	TEMPERATURE[a]	CONDITION	TENSILE STRENGTH	ELASTIC LIMIT (E) PROPORTIONAL LIMIT (P) YIELD POINT (Y)	ELONGATION	REDUCTION IN AREA
	° *C.*		*1000 lbs./sq. in.*	*1000 lbs./sq. in.*	*Per cent*	*Per cent*
IRON AND STEEL:						
Armco iron, max. impurities 0.16%		Hot-rolled	42–48	26–37 (Y)	38–22	78–65
		Cold-rolled	60–63	57–59 (Y)	11–7.5	71–66
		Average plate	46	30	28	
Wrought iron			48–53	28–32 (Y)	40–30	45–35
Mild steel, 0.10 C.			46	35 (Y)	37	72
Cast iron		Malleable	35–57	20–45 (Y)	15–5	15–5
		Gray	25–38			
HIGH-SILICON IRON:						
Duriron, 14.5 Si		Cast	10			
CHROME-IRON ALLOYS:						
Group 1· Crucible Stainless A		1800° Q, 572° T	223	194 (E)	9	28
Group 2:						
Ascoloy 33, 12–16 Cr		Annealed	72–85	40–50 (E)	32–37	70–78
Crucible Stainless 12, 11.5–13 Cr		Annealed	68	30 (E)	11	28
		1750° Q, 750° D	166	116 (E)	22	68
Enduro S, 12.5–14.5 Cr		Hot-rolled	100–110	75–85 (Y)	5–8	
		Box-annealed	85–95	60–70 (Y)	14–18	
Group 3:						
Crucible Stainless 18, 17–19 Cr		Annealed	72	45 (E)	30–35	60–70
Enduro A, 16.5–18.5 Cr		Hot-rolled	85–95	60–80 (Y)	9–11	
Group 4:						
Ascoloy 55, 26–30 Cr		Annealed	75–100	45–60 (E)	25–35	45–65
		Cast	40–80	30–70 (E)	2–5	2–6
	1150		5			
Crucible Stainless 24, 23–30 Cr		As rolled	80–90	55–65 (Y)	22–27	40–50
Duraloy, 27–30 Cr		Cast	40–50	30–40 (E)	1–0	2–0
		Rolled	80–90	60–65 (E)	27–10	45–15
Calite S		Rolled	95		24	49
	900	Rolled	5		67	96
CHROME-NICKEL-IRON ALLOYS:						
Allegheny metal, 17–20 Cr, 7–10 Ni		Annealed	90	45	61	75
	1100		11		45	67
Enduro KA2, 17–20 Cr, 7–10 Ni		Annealed	85–90	33–38 (Y)	55–60	
Rezistal No. 2, 17–19 Cr, 8–10 Ni, 1–3 Si		Softened	90–100	45–55 (Y)	55–65	50–70
		Hot-rolled	150–175	85–105 (Y)	30–40	30–40
Ascoloy 44, 22–25 Cr, 10–13 Ni		Annealed	100		60	68
	1100		13		33	47
Rezistal No. 4, 17–18 Cr, 25–26 Ni, 2–3 Si			109–113	62–90 (Y)	38–31	53–49
Rezistal No. 7			91–129	45–83 (Y)	33–16	41–28
Calite A		Cast	67		2	3
	1100	Cast	15		16	31
Calite E		Rolled	89		61	76
	900	Rolled	25		35	56
Calite N		Cast	51		2	1
	1100	Cast	15		7	7
Calite B		Cast	63		0	0
	1000	Cast	18		4	4
PURE METALS:						
Lead		Cast	2			
		Rolled	3			
Aluminum		Cast	12–14	8–10 (P)	29–15	36–22
		Annealed sheet	13.5	8.5 (P)	23	25
Copper (99.6%)		Cast	25		20	60
		Rolled	50	20 (P)	5	8
		Annealed	35		50	60
Nickel (98.5%)		Cast	38	24 (Y)	6	6
		Rolled	92		11	
		Annealed	76		35	
NON-FERROUS ALLOYS:						
Monel metal, 65 Ni, 30 Cu, 5 other metals		Cast	65–80	30–40 (Y)	25–35	
		Hot-rolled	89–83	42–60 (Y)	46–37	
Alcumite, 87.5 Cu, 7.5 Al, 3.5 Fe, 1.5 Ni		Cast	75	25 (Y)	30	35
		Hot-rolled	85–100	40–60 (Y)	25–15	25–20
		Annealed	76	28 (Y)	40	45
Ambrac, 75 Cu, 20 Ni, 5 Zn						
Barberite, 88.5 Cu, 5 Ni, 5 Sn, 1.5 Si		Cast	50–65	44–49 (Y)	3–13	
Everdur, 95 Cu, 4 Si, 1 Mn		Cast	50	30 (E)	24	35
		Cast and forged	64	40 (E)	54	60
		Hot-rolled rod	75	48 (E)	56	53
		Cold-drawn rod	110	70 (E)	15	22

[a] Room temperature where not specified.

Chrome-iron alloys are attacked by sulfuric acid, but it has been found that they sometimes stand up well in handling acid mine waters, probably owing to the presence of considerable amounts of iron or copper sulfates in the acid water. Pump impellers, shafts, and casings have given very good service in many cases.

At chromium contents as low as 12 per cent the chrome-iron alloys are resistant to the attack of sulfur compounds. Alloys of the composition noted are used in the petroleum industry for such equipment as oil-valve parts and bubble-tower caps.

Chrome irons are now available in a wide variety of forms, including seamless tubing. They may be forged, cold-rolled, stamped, and deep-drawn, either hot or cold, and may be welded by either the electric arc or the oxyacetylene flame. Alloys falling in the first three groups give welds which tend to be brittle but are subject to improvement on heat treatment, the third class being most satisfactory. The high-chromium alloys of the fourth group can be welded only with difficulty, the welds showing brittleness which is not removed by heat treatment. Equipment fabricated from this type of material should be riveted or bolted, whenever possible, instead of welded. In general, equipment for high-temperature work should be welded because of the tendency of rivets to loosen up, while other equipment should be riveted if possible. Alloys of the third group rivet most satisfactorily, but even in using this type of material care should be exercised that the riveting temperature is not too high.

Chrome-Nickel-Iron Alloys

Developing subsequent to the "stainless" alloys, the chrome-nickel-iron combinations have shown great potentialities for the chemical engineer. The best known type of material is the 18 per cent chromium, 8 per cent nickel alloy, which appears as the English Staybrite Steel, as Allegheny Metal, and as Enduro KA2. Seamless tubes of these alloys are finding important uses in high-temperature, high-pressure oil-cracking stills. They resist nitric acid, mixed acids, 45 per cent boiling phosphoric acid, boiling acetic acid, and boiling caustic solutions, as well as fruit acids and lactic and fatty acids. They are finding wide use in the chemical industries, in dairy equipment, in the manufacture of soft drinks, in the cooking and packing equipment of large canneries, and in equipment such as evaporators and crystallizers for the manufacture of citric and tartaric acids from cull oranges and lemons.

One of the important uses of the 18 chromium–8 nickel alloy is for drums for shipping nitric acid, which have been recently approved. Two other specific applications are in sulfite digesters and in dyeing tanks.

High-chromium, high-nickel alloys containing approximately 3 per cent silicon are included in the line of Rezistal steels. An alloy containing 17 per cent chromium, 25 per cent nickel, and 3 per cent silicon is used for carburizing boxes and furnace parts, and gives an extremely long service life. Another alloy approximating in composition 25 chromium–20 nickel-3 silicon can be used for boiling acetic acid in all concentrations, and for boiling sirupy phosphoric acid. Alloys containing appreciable amounts of silicon are said to be superior in their resistance to sulfur dioxide and to acid mine waters.

Chrome-nickel-iron alloys are available in many standard forms, are very ductile and tough, and are completely non-hardening. This last quality is extremely valuable from the standpoint of fabrication, since these alloys can be welded without any tendency for the weld to become hard and brittle. These alloys may be forged, cold-rolled, and stamped and deep-drawn, either hot or cold, but are somewhat difficult to machine. Welding may be done with either the electric arc or the oxyacetylene flame.

Pure Metals Other than Iron

Lead—Wherever sulfuric acid is handled, lead is the traditional resistant material of construction. Miles of lead pipe are used in both the chamber and contact processes for the manufacture of this acid, and the former process depends upon lead as the lining for the chambers. Sulfuric acid up to 60° Bé. concentration has only a slight action on lead even when heated nearly to the boiling point, and concentrated acid (96 per cent) still has but little action in the cold.

Pure chemical lead has very little strength. Hard leads, containing antimony or other alloying substances, have greater strength but less resistance to corrosion. Where both strength and chemical resistance are required, special Crawlproof lead is used, which is chemical lead reënforced with hard lead. For still higher strength requirements, lead is used as a lining for iron or steel equipment. This will be mentioned in a subsequent section dealing with metallic coatings.

Lead also finds a limited use in contact with acids other than sulfuric, on the grounds of serviceability and economy in spite of gradual corrosion over extended periods of time. For example, lead is used with cold concentrated nitric acid and with cold dilute hydrochloric acid, whereas dilute solutions of alkalies have but a slight effect on it. Lead is practically the only metallic material available for handling moist ammonia. It finds other uses in the general handling of phosphoric acid and acid sulfite liquors, in evaporators for alum, pumps for concentrated acetic acid, and in contact with various other substances.

One of the great advantages of lead for chemical plant equipment is that a competent lead burner can fabricate, in the plant and on short notice, almost anything under the sun, while lead equipment can likewise be speedily repaired in the same way.

Aluminum—This metal is resistant to the action of pure acetic and pure nitric acids, sulfur compounds, lactic, citric, tartaric, and the fatty acids. Evaporators for pure acetic acid are frequently built of aluminum, as are the drums used in the shipment of this substance. Aluminum is used in Europe for the shipment of air-nitric, but cannot be used for nitric acid made from Chile saltpeter because the metal is attacked by the impurities present. In the petroleum refining industry aluminum is used in equipment subject to sulfur corrosion—for example, bubble-tower caps, heat exchangers, and the roofs of petroleum-storage tanks. Calorized (aluminum-surfaced) tubes are used in cracking stills; this will be discussed in a subsequent section on metallic coatings. The property of resisting the attack of sulfur compounds makes aluminum a valuable material in the rubber industry, where it is used in making mandrels for inner tube manufacture, and in molds for all sorts of rubber articles. Turpentine stills and stills for the destructive distillation of wood are also constructed from aluminum.

Although aluminum is not the most resistant material available for the purpose, it is used extensively as stretcher rods for handling rayon during washing and drying. Aluminum stands up well in the dairy and food industries, where the fact that its salts are non-poisonous makes it particularly valuable, while the colorless character of its salts similarly gives it an advantage in such industries as the making of fine candles, the drying of dyes, and the manufacture of varnish. Aluminum is fabricated into crystallizing pans for citric and tartaric acids, condensers and deodorizers for vegetable oils, milk tanks and coolers, and kettles of various types, to mention some of its specific applications.

Aluminum is obtainable in a large number of standard forms, and is fabricated with extreme ease. In castings for chemical equipment silicon or manganese hardeners are usually used to alloy the aluminum. Cast forms are in general somewhat less resistant than wrought forms.

Copper—The traditional field of alcohol distillation, both on a private and on an industrial basis, is associated with copper equipment. This metal stands up well against hot, dilute acetic acid, and crude acetic, containing formic acid, which cannot be distilled in aluminum, is usually handled in copper. This material is also used to some extent for caustic. Deoxidized copper tubes have had quite a vogue in sugar evaporation, and copper dairy equipment is used extensively. Two special uses of this metal are the handling of benzoic acid vapors and of para-nitrophenol. Copper, however, is becoming more important in the form of alloys than in the pure state. These alloys include the brasses, bronzes, aluminum bronzes, monel metal, etc.

Pure copper is available in sheets, tubing, rod, and other forms, and is easily machined and fabricated.

Nickel—The dairy industry uses large amounts of nickel for tanks, preheaters, and pasteurizers. Much food-canning equipment is also constructed of nickel, which is resistant to acetic and fruit acids. Although nickel is ordinarily considered as readily attacked by sulfur compounds, it is used extensively for strainers in oil wells producing high-sulfur oil because nickel strainers give long life and do not plug up. Nickel evaporator tubes and baskets and whole evaporators of nickel have been constructed for use on caustic. Recently nickel has been adopted for parts of the regenerative system of a well-known zeolite water softener, because of its resistance to corrosion by the concentrated salt solutions used. Nickel is also valuable in the handling of benzoic acid vapors, chloroacetic acid, and rayon dope.

Nickel is available in the standard, and in many of the less usual, fabricated forms, including tubing. It has excellent mechanical properties and can be worked and machined.

Non-Ferrous Alloys

Monel Metal—This is an extremely important material. On one hand it is resistant to dilute sulfuric acid, and is therefore used widely in pickling equipment—as tanks, crates, baskets, acid pumps, mixer shafts, and ventilator hoods, ducts, and fans. On the other hand it is an excellent material for the handling of caustic, and is used accordingly for severe duty as caustic fusion pots in dye manufacture and for equipment handling strong solutions in the manufacture of caustic. Evaporators, crystallizers, and filters for this purpose are built in whole or in part from monel metal. Similar equipment is built for the concentration of fruit juices and of black liquor from sulfate paper processes. Varnish kettles, liners and flights in salt driers, centrifugals for clarifying fruit juices, and filter cloth for a wide range of purposes are made from this material. Monel metal has largely replaced wood as a construction material for dyeing vats. It is used for tanks and pumps for hydrofluoric acid, in bleaching equipment for textiles, as still plugs for high-temperature high-pressure oil-cracking stills, and extensively in the food industries for processing and packaging equipment.

Monel metal has very good mechanical properties. It can be readily machined, and is available in a remarkable range of fabricated and machined forms.

Special Bronzes—It is impossible, within the scope of this article, to mention all the various alloys represented in the brass and bronze groups. Specific reference to four particular alloys of interest to the chemical engineer will be made. Alcumite is a well-known representative of the aluminum-bronze group; Ambrac is a copper-nickel-zinc alloy; Barberite contains copper, nickel, tin, and silicon; and Everdur is a manganese-silicon bronze.

Alcumite finds important applications in pickling equipment, in handling acid mine waters, and in the handling of practically all corrosive vapors except strong nitric acid fumes. Alcumite and other alloys of the copper-aluminum-iron or copper-aluminum series can be cast, rolled into any desired forms, and readily machined. These alloys cannot be welded.

Ambrac is used in handling hypochlorite bleach solutions, for salt evaporator tubes, and for pickling equipment or other dilute sulfuric acid service, to mention some of its specific applications in chemical engineering processes.

Barberite is recommended by its makers for use with any strength of sulfuric acid at temperatures up to 96° C., and for general service in contact with caustic solutions, arsenious, tannic, crude salicylic, and the fatty acids, and many organic compounds, including formaldehyde, phenol, acetone, and carbon tetrachloride. It is available in valves used in handling sulfuric acid and for use in special castings.

Everdur is a new type of alloy with an approximate composition of 95 per cent copper, 4 per cent silicon, and 1 per cent manganese. It has good resistance to sulfuric acid, either cold up to 95 per cent or hot up to 50 per cent, in the absence of oxidizing agents. Everdur is also resistant to all strengths of hydrochloric acid in the absence of air, and finds considerable use in this field of service. Everdur may be cast, fabricated into a variety of forms, machined readily, and welded by either the electric arc or the oxyacetylene flame.

Stellite, a cobalt-chromium-tungsten alloy, is extremely resistant to attack by many chemicals, but cannot, because of its cost, be considered from an economic standpoint for industrial chemical equipment, except for small valve or pump parts. Its unusual hardness gives it important applications as an abrasion-resistant surfacing material, which will be discussed in a later section. Alloys have been developed from stellite for handling hot, concentrated hydrochloric acid.

Zilloy is a high-zinc alloy recently developed for roofing and siding in industrial plant construction.

Rare and Precious Metals

Platinum-gold and palladium-gold spinnerets have been used in the rayon industry, their high first cost being largely offset by their intrinsic value when scrapped. Tantalum is entering this same field. This material also resists attack by hydrochloric and nitric acids, aqua regia, dilute sulfuric acid, and caustic alkali solutions.

Silver has been used in some instances for the distillation of acetic acid, and is generally used in the manufacture of acetanilide.

METALLIC COATINGS

When a certain metal possesses specific corrosion resistance valuable in a given process, it may frequently be applied as a coating upon some base material when either the cost or the mechanical properties of the pure metal place it out of the running for use by itself. Metallic protective coatings suffer, however, from the fundamental disadvantage that, once broken through at even a minute point, they may cause the ruin of a whole piece of equipment. This puts metallic coatings upon the same basis as enamel ware. At present there seem to be more proposals than achievements in the field of metallic coatings for use in the process industries. Some of the more important developments will be mentioned, however.

Coatings Produced on Metals by Chemical Action

Parkerizing, or the formation of a surface film of iron phosphate on steel or iron, is not, in general, important from the standpoint of resistance to corrosion in chemical engineering processes though it affords excellent protection against atmospheric corrosion.

The formation of a nitrided layer on the surface of steel is important from the standpoint of abrasion resistance, and also to some degree from that of resistance to weak corrosive agents.

Coatings Produced by Diffusion of Metal, Spraying, or Dipping

Calorizing is the process of coating steel with a thin layer of aluminum which is bonded to the steel through an intermediate region in which the aluminum and iron are alloyed.

Calorized steel tubes have the mechanical properties of steel combined with the surface properties of aluminum. They are employed in oil-cracking stills because of their resistance to oxidation and general corrosion up to a temperature of 900° C. Other refinery equipment, such as valves, burner tips, header plugs, and bubble tower caps, are also calorized. Salt and lead hardening pots for steel are also calorized to resist the attack of high-temperature furnace gases.

Chromized steel castings are available for high-temperature work. These present the surface resistance to oxidation of high-chromium alloys, but are less expensive than complete alloy castings.

Galvanized iron is used as a cheap material in handling many neutral salt solutions.

Lead may be deposited on iron or steel by *hot dipping* or *spraying*. Other metals are also applied by spraying, by processes such as the Schoop method. A general defect of this type of application when regarded from the standpoint of resistance to severe corrosion conditions is the tendency toward small discontinuities in the completed coating.

Coatings Produced by Casting, Welding, or Rolling

Chrome-iron and chrome-nickel-iron alloys may be welded to cast iron or steel. A relatively thin lining of either of these types of material may thus be used in a heavy-pressure vessel or in ordinary equipment to obtain corrosion resistance at reduced expense. This process offers apparent possibilities, although it has not yet been worked out to the point where satisfactory results can be guaranteed.

It is possible to weld stellite to cast iron or steel, building up a thin, continuous layer of this material on small articles for which the advantage of such a surface overbalances the cost. It is not generally applied in such a manner for the purpose of resisting corrosion, but it is used in the construction of wearing parts because of its extreme hardness and resultant resistance for abrasion. Hammers in hammer mills, grinding rings in roll mills, pulverizer plow arms, screw conveyor edges, drag chain shafts, and rider blocks are all faced with stellite. This material is applied preferably by oxyacetylene welding.

The lining of equipment with lead has been developed to the point where very good results are consistently obtained. Lead-lined pipe, flanges, valves, stirrers, agitators, tanks, coils, kettles, stills, pumps, evaporators, drums, etc., are quite standard for processes in which lead is indicated as the proper material. Larger surfaces are now lead-lined by processes which give good adherence of the coating to the base metal, such as the Zeitler wire-mesh reënforcement process, and which are also free from minute holes.

Aluminum is applied to the surface of duralumin or other aluminum alloys to produce materials of the Alclad or Alautal type, extremely light in weight, of excellent mechanical properties, and with the surface resistance of pure aluminum.

Coatings Produced by Electrodeposition

Electroplated deposits are not ordinarily relied upon to stand severe chemical corrosive action. In some cases, however, silver- and nickel-plated coatings have been utilized, as in the silver-plated copper buckets used for photographic dope. Recently there has been much talk about the possibilities of chromium plating, but many of the predictions have been proved somewhat over-optimistic. Chromium plating has been able, however, to materially reduce the corrosion in evaporator tubes handling waste sulfate pulp liquor, and the corrosion due to sulfur attack in oil cracking chambers.

Zinc and cadmium plating are much used for resistance to atmospheric corrosion, but are not suitable for many purposes where they will be exposed to more severely corrosive conditions.

Conclusion and Acknowledgments

In this necessarily very sketchy review, very little detailed information concerning any one material could be included for reasons of space. Anyone interested in the general field of materials of construction will find more specific details available in the appended references to the recent literature, and from the following concerns which supplied information and assistance to the writer during the preparation of this article: American Rolling Mill Company, Duriron Company, Allegheny Steel Company, Central Alloy Steel Company, Industrial Welded Products Company, Crucible Steel Company of America, Duraloy Company, Calorizing Company, National Lead Company, Aluminum Company of America, International Nickel Company, American Brass Company, Haynes Stellite Company, Barber Asphalt Company, and New Jersey Zinc Company.

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New Synthetic Ammonia Plant for Soviet Union—The Amtorg Trading Corporation, which represents the Soviet Union in the United States, announces that plans for the construction in the Soviet Union of a factory estimated to cost ten million dollars and to produce synthetic ammonia fertilizers are being prepared by the Nitrogen Engineering Corporation, of New York.

Renaissance of the Absorption Refrigeration Cycle[1]

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THE earliest machines for producing refrigeration mechanically were of the type where operation depends upon the absorption of the refrigerant gas in a liquid. The possibility of an absorption refrigerating cycle will therefore be perceived to begin with the discovery of gases which dissolve abundantly in readily obtainable liquids of low vapor pressure at ordinary temperatures. Thus ammonia, discovered by Joseph Priestley in 1774, and methylamine are possibilities to be considered in designing an absorption cycle wherein the dissolved gas in water may be driven out of one vessel (absorber-generator) and collected in a second vessel (evaporator), hermetically sealed to the first. Cooling of the generator causes the vessel first mentioned to function as an absorber and the liquid refrigerant in the evaporator is caused to evaporate, thereby cooling the evaporator. When the refrigerant has completely returned to the cooled absorber, heat is again applied to the absorber, whereupon it functions as a generator and the cycle of operations is recommenced.

Principle of Absorption Refrigeration

The general principle upon which the functioning of a typical absorption refrigerating machine rests is clearly the difference in solubility exhibited by gases in cold and hot absorbing liquids of relatively low vapor pressure. A low vapor pressure of the solvent liquid is desirable, since operation is simplified when during the heating cycle as little of the solvent as possible is carried over to the evaporator.

Evidently the absorption machine is in principle exceedingly simple, requiring but two pressure vessels with means for applying cooling water, a certain amount of piping, and no moving parts are involved. It will be made clear below that the effort to produce an entirely automatic absorption machine capable of "sensing" its cooling and fuel needs, at such times and in such amounts as are required to maintain a specified temperature within a refrigerator, reasonably independent of the temperature of the surroundings, has resulted in a few accessories being added to the simple equipment described above. The automatic self-regulating absorption machines now on the market have already arrived at the point, however, where the inherent simplicity of operation and structure is retained with a minimum of simple control apparatus of a highly ingenious design.

The forms of energy which may be used to operate the absorption machine are as numerous as the sources of energy available. Heat is the form of energy directly applied to the generator, and this may of course be obtained electrically or from the combustion of gas, oils, etc. An absorption type of machine can therefore be adapted to many diversified requirements, although the machines on the market at present operate with heat from electricity and gas only. The development of machines to operate with liquid fuel will eventually be completed and already one development (refrigerator car) is employing liquefied propane in tanks as a source of fuel.

The cooling medium thus far used has been water. The companies interested in absorption refrigeration development have been designing air-cooled units for a considerable time and quietly testing the performance under all possible conditions of use. It is a safe prediction that within a few years at least air-cooled machines will be available, which from the point of view of efficiency of operation and cost will be everything that can be desired. The water-cooled machine is preferred by the writer whether the refrigerating unit is of the absorption or motor-compressor type. A few of the reasons for this preference are that the unit is more compact, somewhat more efficient, more quickly responsive to sudden changes in outside temperatures, and less liable for service when once installed.

The absorption machine thus far is the more common type wherein a liquid is used to absorb the refrigerant gas. There are, however, other and later types equally important and interesting. There has been an attempt to use a solid salt, such as ammonium nitrate[2] or ammonium thiocyanate, either of which is exceedingly soluble in ammonia. Now it is well known that the vapor pressure of the solvent of a salt solution is lower than the vapor pressure of the pure solvent. With the salts mentioned, however, the vapor pressure of ammonia is tremendously lowered. There is presented, therefore, the prospect of obtaining not only an absolutely nonvolatile solvent for the absorption cycle but a solvent (ammonium nitrate) which absorbs heat or cools when the refrigerant dissolves, thereby leading to increased efficiencies. There are, of course, difficulties still to be overcome before the advantages of this type of absorption machine may be realized. The difficulties would probably yield, as usual, to sustained effort on the part of those especially apt in perceiving the practical applications of physico-chemical principles.

The recent developments in the knowledge of the phenomena of adsorption (a special term for absorption on surfaces) and adsorptive materials have led to the introduction of still another type of absorption machine, which might very appropriately be termed the "adsorption" machine. This machine operates by virtue of the fact that a gas such as ammonia, absorbed, or better "adsorbed," by charcoal is retained very tenaciously and at very low pressures. The application of heat increases the pressure and the ammonia may be driven out and condensed to be reëvaporated and readsorbed in the charcoal (adsorbent).

There are many adsorbents, but one whose application has been found especially well suited is silica gel. The preparation of this material was developed by Walter A. Patrick, of Johns Hopkins University, and is manufactured by the Silica Gel Corporation, which has assigned rights for the use of the material in small units to the Copeland Products Company, of Detroit. The latter company, it is understood, is developing practical units for household application. Meanwhile, the substance has been used in an interesting application—that of the artificially refrigerated freight car.[3]

Silica gel is a hard, glasslike material composed of pure silicon dioxide. It is produced by precipitation from sodium silicate and the process of its manufacture has been continuously improved to the point where a considerable augmentation in the adsorptive characteristics has been realized. There are other gels also which may in time be brought into a preferred physical state especially useful for certain important specific purposes.

There remains to be mentioned the possibility of employing in a refrigeration cycle the chemical substances which

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[1] Received February 21, 1929.

[2] See, for example, Keyes, U. S. Patents 1,258,017 and 1,267,772 (1918).

[3] Hulse, *Refrigerating Eng.*, **17**, 41 (1929).

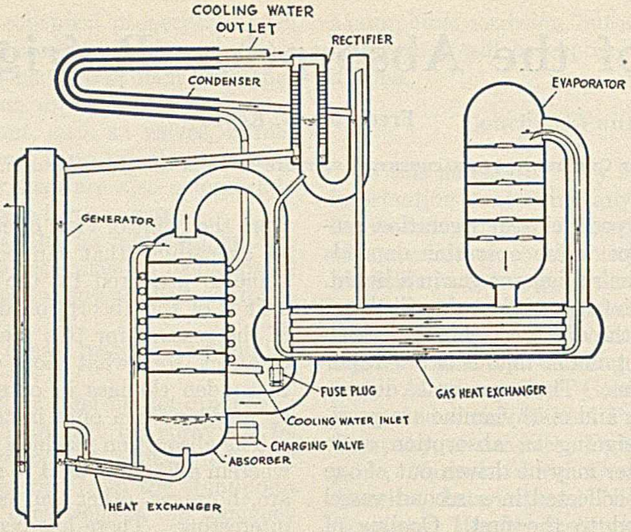

Figure 1—Diagram of Electrolux Servel Refrigerator

form "associated compounds," among which hydrates and ammines ($BaCl_2.8NH_3$) are examples. Thus the ammonia pressure over the latter compound has a relatively low pressure at ordinary temperatures and is readily driven out by heat to be reabsorbed when the salt is cooled. It happens that the rate of absorption of ammonia and other factors make barium chloride not the most desirable of salts to choose for the purpose, but there are other salts which form ammonia addition compounds, and one practical household refrigerating machine[4] employs a combination of absorbing elements based on the addition-compound-forming property of certain salts.[5] The special difficulties of poor heat conduction, slow absorption rate, permanency of preferred physical state, and capacity have been entirely overcome without sacrificing in any way the important advantages presented in the use of such addition compounds. Among the advantages to be noted is the possibility of employing ammonia, in many respects an ideal refrigerant, in the anhydrous condition, thereby eliminating entirely any form of rectifier as with a water absorption unit. The use of anhydrous ammonia incidentally permits the use of copper tubing in the construction of the unit, and the compact and fireproof nature of the absorbent is a further advantage.

Improvements in Small Water Absorption Units

In 1900 a patent was issued to Geppert[6] in which a novel idea was incorporated in the design of the water absorption machine. It was proposed, in essence, to convert the well-known water-ammonia absorption machine into a constant-pressure system by adding air or a permanent gas. Geppert's embodiment of the idea shows a pump for circulating the air over the liquid ammonia in the evaporator, bringing about a "forced" or accelerated evaporation. The inert gas also functions as a kind of expansion valve, since the ammonia may be condensed by the pressure of the inert gas and passed directly to the receiver, or even the evaporator, depending on the size and design of the machine.

Comparatively recently Geppert's idea has received modification at the hands of Platen and Munters, who made use of the small density of hydrogen relative to ammonia vapor (1 to 8.5) to bring about a natural circulation of the inert gas over the surface of the liquid ammonia in the evaporator. The circulating pump is thus eliminated and the water absorption machine converted into a continuously operating machine as contrasted with the older intermittent distillation, water-absorption cycle unit.

The constant-pressure hydrogen-water absorption machine as designed by the Electrolux-Servel Company is represented in diagram in Figure 1. The function of each part of the machine is labeled in the figure and circulation of the cooling water, the ammoniacal liquor, liquid ammonia, ammonia vapor, and hydrogen may be readily followed. Through the central tube of the generator a Bunsen flame is allowed to burn, causing the evaporation of the ammonia from the strong liquor siphoning into the lower part of the generator from the absorber. The weak liquor from the generator passes by gravity from the generator to the upper part of the absorber, spreading itself over the trays, which are cooled by water flowing continuously in the coils surrounding the evaporator. The cooled strong liquor collecting in the bottom of the absorber passes back to the generator through

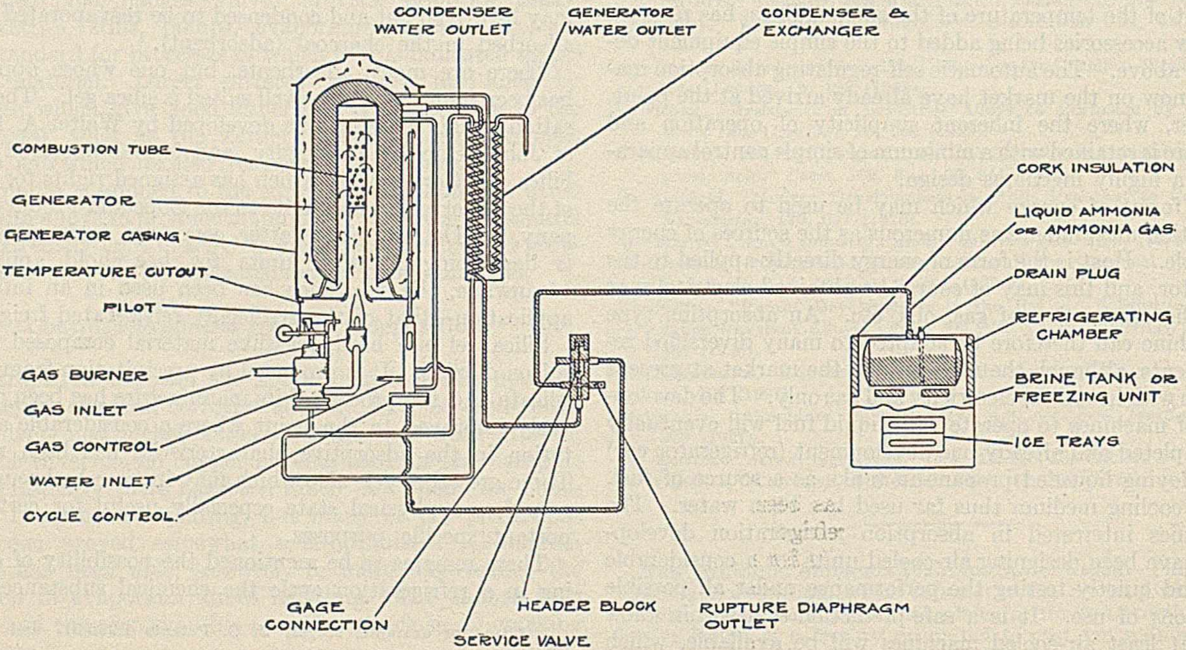

Figure 2—Diagrammatic Drawing of Ice-O-Lator

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[4] Ice-O-Lator unit, manufactured by the National Refrigerating Company of New Haven, Conn.

[5] Keyes, U. S. Patents 1,622,519 to 1,622,523, inclusive (March, 1927).

[6] Geppert, U. S. Patents 622,690 (November, 1900) and 780,096 (January, 1905).

a heat exchanger to be deprived of its ammonia in the generator. The ammonia evolved in the generator condenses at the temperature of the condenser and under the pressure exerted by the inert gas. After rectification, the liquid ammonia is led to the evaporator flowing over the trays, where the vapor of the ammonia mixes with the hydrogen forming an ammonia-rich mixture. This mixture is heavier than the corresponding mixture in the absorber, since the hydrogen in the latter has been deprived of its ammonia by absorption in the weak liquor flowing over the trays. A natural circulation due to difference in density accordingly sets in, the ammonia-rich mixture sinking in the evaporator to be replaced by relatively ammonia-free hydrogen entering at the top of the evaporator from the absorber.

It is easily seen that there results from this design a machine capable of continuous operation, completely or hermetically sealed, and possessing no moving or wearing parts. Of course, to control the amount of refrigeration delivered from such a machine to suit climatic or such conditions as the user desires, certain automatic control devices are required. Provision must also be made for automatic safety features, all of which have been worked out satisfactorily.

Before entering into the operation costs of the absorption machines, one other type already referred to will be briefly described. It should be stated also that a considerable number of different types of absorption machines have been reported especially designed for the household field. Many of these are adaptations of the old intermittent water-absorption type. The present article would be over-extended, however, if these numerous units were described in detail. It may be remarked that no household machine of the purely adsorptive type is yet available for public purchase. A refrigerator car, using an adsorptive cycle, has been already mentioned and will again be referred to in concluding the paper.

Ammine-Compound Absorption Machine

The proposal to employ an addition compound in a refrigerating cycle seems to have been first made by Puplett and Rigg.[7] No practical utilization in the form of a marketed machine appears to have been made until the appearance of the Narco machine[8] in Boston in 1923.

Successful utilization of the ammine-forming salts in a refrigerating cycle depends on the existence of a salt ammine which possesses the proper pressure-temperature relation. Thus an ammine whose ammonia pressure was too high at ordinary temperature (ammonia boils at 32° F. under a pressure of 65 pounds) would be impractical for producing temperatures low enough for the freezing of ice cubes, the preservation of ice cream, etc. On the other hand, one whose temperature of decomposition was too high would endanger the stability of the ammonia or make the refrigeration cycle inefficient owing to the excessive amount of heat required for operation. Two salts which are suitable are calcium chloride and strontium chloride, the former being preferable from the point of view of cost.

The proper choice of salt settled, there remains the development of a process of putting the salt in the preferred physical state. Among the more important factors involved in using an ammine-forming salt may be mentioned the large volume change occurring when the ammine passes to the salt during the decomposition or heating part of the cycle, the maintenance of a desirable porosity to permit easy diffusion of the refrigerant throughout the material, the avoidance of segregation in the material, and the elimination of the tendency of fine particles of the salt being carried out of the generator by the rapidly moving gas stream. The material is characterized by poor heat conductivity and the design of the generator must be such as to permit a uniform heating of the ammine throughout the generating part of the cycle, as well as uniform cooling during absorption. If a good design is not realized, local overheating will (at 750° F.) gradually decompose the ammonia, resulting in a serious lowering of the efficiency of the refrigerating cycle.

Assuming that the problem of putting the ammine in a preferred physical state by the addition of suitable substances and subsequent treatment is solved, together with the working out of an efficient generator, there exists the basis for a simple refrigerating unit. A rectifier is not required, for anhydrous ammonia of very high purity is circulated. Further, no moving parts are needed with their inevitable wear and ultimately noisy functioning.

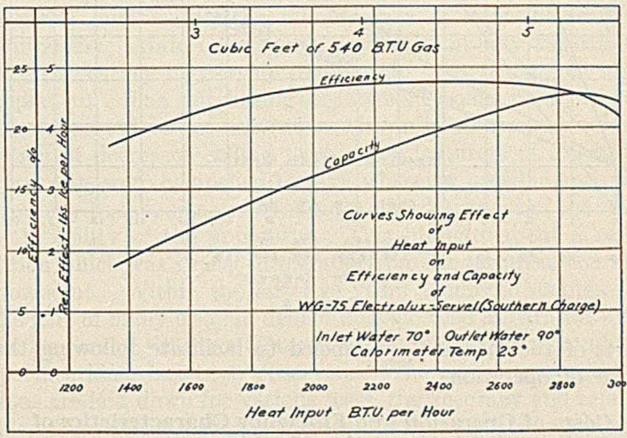

Figure 3

The automatic control of the cycle of operations is the remaining portion of the task in realizing a long-lived, noiseless, and cheaply operated refrigerating unit. The cycle of operations to be automatically performed consists of the turning on of the gas (or electricity) at the moment that the refrigerant has been completely absorbed by the generator or, if the temperature of the refrigerator is sufficiently low, the turning on of the gas must be responsive to a temperature-controlled signal. In any event, at the instant the gas is lighted the cooling means must be transferred from the generator to the condenser. At the conclusion of the heating period, which must be timed to just empty the generator of its refrigerant content, the gas must extinguish and the cooling means transfer from the condenser to the generator, which now becomes an absorber.

The refrigerator box interior once set for a desired temperature (45° F.) should not deviate more than a few degrees (±2° F.) night or day independently of the temperature prevailing outside the refrigerator. Of course, if the temperature of the room falls to zero, special provision would have to be made to heat the interior of the refrigerator box. In several instances coming under the writer's attention this has been done by suitably connecting a carbon filament lamp into the regulating circuit of the refrigerating unit.

Suffice it to state that the marketed machines of the adsorption type are entirely automatic, self-regulating, and protected from the consequences of accidental failures in either gas or other energy applied to heat the generator, or the cooling means. This has been rendered possible by the development of extraordinarily simple and ingenious devices, with the result that the absorption machines are reliable, efficient, durable, silent, and easily serviced. A diagram of one of the Ice-O-Lator units is given in Figure 2, where the

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[7] Puplett and Rigg, British Patent 507 (November, 1889).

[8] The Narco machine was taken over as a subsidiary (National Refrigerating Co.) of the Winchester Repeating Arms Company in 1925 and since marketed under the name "Ice-O-Lator."

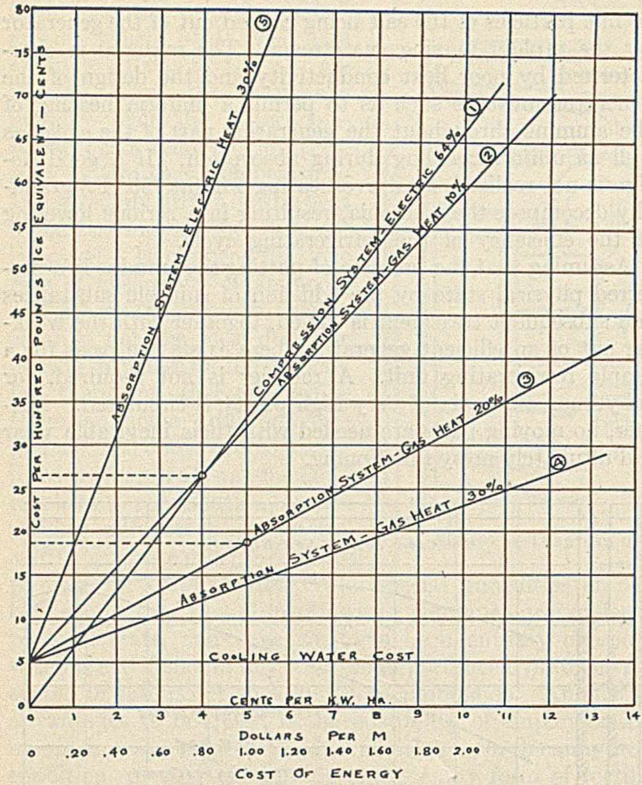

Figure 4

parts of the machine are labeled to facilitate following the cycle of operations.

Costs of Operation and Efficiency Characteristics of Absorption Machines

The data presented are from tests on two types of refrigerating units—the Electrolux,[9] hydrogen-water-ammonia absorption, continuously operating unit, and the Ice-O-Lator intermittent automatic refrigerating unit. The heat input–efficiency[10] capacity chart for cooling water at 70° F. for the Electrolux unit is shown in Figure 3. It will be noted that both curves, efficiency-heat input and capacity-heat input, show a maximum. The maximum in the former is, however, very flat, showing but a relatively small variation in efficiency between an energy input of 1800 B. t. u. per hour and 2600 B. t. u. per hour. The capacity, on the other hand, shows a more abrupt maximum at 2900 B. t. u. per hour. Over a considerable range of the variables, however, the capacity increases nearly linearly with increasing energy input.

Precise figures relative to the effect of varying the temperature of the inlet cooling water, for units of specific design, are not available for the Electrolux unit. As with every refrigerating device, however, whether of the absorption or compression type, the refrigerating effect diminishes as the temperature of the cooling means increases.

The cost of operation for the Ice-O-Lator unit may be obtained from Figure 4.[11] Here the cost of refrigeration based on 100 pounds of ice equivalent refrigerating effect is given for absorption machines of five different efficiencies; three gas units (Ice-O-Lator) and one electric absorption unit (Ice-O-Lator) are compared with data based on the results of tests on a number of compression units. The "20 per cent" gas unit may be taken as an average, and it is evident that the cost of operation is more favorable than either the compression unit or the electrically operated absorption unit.

It is obvious that the average householder is not necessarily greatly concerned with costs of operation. Service costs might easily wipe out a considerable difference in running charges. It is, however, precisely in the element of durability and freedom from service that most is to be expected from the absorption machines, because of the absence of an electric motor and wearing parts. It may be added that, while the absolute cost of operation of the household machine as compared with silence of operation and freedom from service, may not primarily interest the householder, the grocer, butcher, florist, drink dispenser, etc., are concerned with costs, which again makes for interest in the gas-operated absorption unit.

Adsorption Freight Car Refrigerating Unit

In conclusion, the attention of the reader is again called to the very interesting article by Hulse[3] on the artificially refrigerated freight car. There is provided here an example of a system of refrigeration based on the property known as adsorption or surface condensation in which the adsorbent is silica gel. The description, illustrations, and details given by Mr. Hulse are very complete and the results obtained in trial trips are convincing evidence of the splendid results to be obtained by the installation of mechanical refrigeration in freight cars conveying perishable goods. Figure 5[3] is a diagram of the actual mode of installing the unit, and the original article giving complete details should be consulted by the reader interested in this important development.

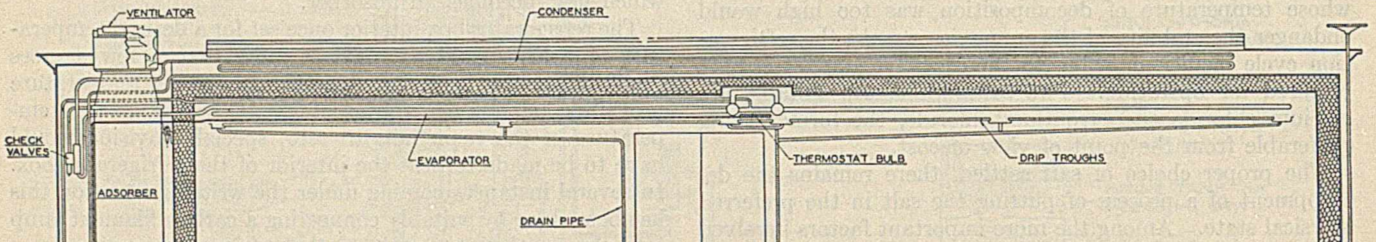

Figure 5—Diagram of Refrigeration Equipment in Car

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[9] Data furnished by Robert S. Taylor, of the Electrolux Company.

[10] The efficiency percentage as used in this paper is the ratio of the energy corresponding to the refrigerating effect realized (energy of melting of one pound of ice times pounds of ice produced) divided by the total energy applied to the unit multiplied by 100.

[11] Hainsworth, *Refrigerating Eng.*, **13**, 245 (1927).

Works Control and Laboratory Equipment[1]

Arthur Schroder

FISHER SCIENTIFIC COMPANY, PITTSBURGH, PA.

> The reason why we are on a more imaginative level is not because we have finer imaginations but because we have better instruments. In science, the most important thing that has happened during the last forty years is the advance in instrumental design.* * *
>
> A fresh instrument serves the same purpose as foreign travel; it shows things in unusual combinations. The gain is more than a mere addition; it is a transformation.—A. N. WHITEHEAD

FOR THE last generation technical control has had for its milestones the development and standardization of scientific testing methods and apparatus. A survey of the developments in the technical control of products, both in the plant and through the laboratory, shows certain marked tendencies:

(1) The producing and consuming public are becoming "scientific-minded," and believe in testing as a means of establishing common basis of exchange of commodities.

(2) Works control equipment is becoming more and more simplified and standardized.

(3) There is an ever increasing utilization of the measurement of one specific physical property of a product, as an index of the quality of that product in each step of its manufacture.

(4) There is now evident a new attitude of coöperation between the manufacturers and users of scientific testing apparatus.

These tendencies will be briefly discussed and then some of the more outstanding developments in the various fields of works control and laboratory apparatus will be described.

A "Scientific-Minded" Public

The World War probably did more for the advancement of the manufacture of scientific apparatus in the United States than did anything else. Our sudden realization of our almost utter dependence upon foreign sources for testing equipment made us aware of the need of such an industry within our own borders. As a result of this, the average man in the street has become interested in science and, as a sequel to this, has carried his interest into his business. Where once a laboratory was considered, like insurance, a necessary evil thrust upon an organization by a manager who wanted to ride a hobby, today we find the average consumer demanding a uniformity in his product which can be guaranteed only by scientific control of its production. The publicity given the Chemical Warfare Service during and immediately after the war has awakened public interest in chemical and allied sciences. This has led to the formation of laboratories in industries in which they were unheard of before the war.

In 1920 the National Research Council[2] listed about 300 industrial research laboratories. This number is now[3] over 1000. The Bureau of Standards[4] reports some 270 commercial testing laboratories. From a more recent private survey, there are in the United States about 5000 industrial laboratories and about 1200 public health laboratories controlling sanitation through water and food analysis. In addition, some 2500 colleges and about 8000 high schools are giving courses in chemistry and allied sciences. The work done in these laboratories is permeating the public to the extent that it now realizes what chemistry can do, and is just beginning to hope, and almost expect, that it can do anything.

With this scientific interest on the part of the public has come an increasing realization on the part of producers of the need of a control laboratory, and also a more recent realization that the laboratory must be responsible for the quality of production.

It was not so long ago that supplies for laboratories were frequently specified by the laboratory and then purchased on the open market through a purchasing department, which was usually under pressure to buy equipment at the cheapest possible price. Rarely did that department realize the intricacies involved in the manufacture of scientific testing equipment. Material was purchased by name only, regardless of the accuracy necessarily involved in a particular piece of apparatus. The purchasing department could hardly have been expected to act otherwise. In order to meet this condition of decreased selling price, manufacturers of scientific apparatus were compelled to save wherever possible and, we are sorry to say, sometimes saved to the detriment of the ultimate utility of the apparatus. This brought about a condition which was almost intolerable from the technical control viewpoint. Within the last five years a marked change on the part of many users in demanding specified apparatus, and on the part of the manufacturer in building up corresponding specifications, has been observed. When definite specifications are laid down for various tests, the accuracy and reproducibility of the tests are increased. But by standardizing the tests and the apparatus along with the tests the cost of the apparatus is greatly reduced, because specially made types are no longer necessary and larger production can be employed. Now the tendency is to incorporate in specifications for equipment only the essentials and leave the unessentials to the manufacturer for his solution.

With the increasing number of laboratories springing up throughout the country, and with this changed attitude, has come a need of a clearing-house for information on methods of testing and testing equipment. This need is being met by an ever increasing number of technical associations. There are now something like 250 trade associations operating technical laboratories of one sort or another for the mutual benefit of their members. Needless to say, the American Society for Testing Materials is the father of them all.

An idea of the scope of the activities of these societies can be obtained from a report of the American Society for Testing Materials,[5] in which almost 2000 pages covering 340 standard specifications have been published. Since that time some 200 more[6] specifications are in the process of development. These cover the testing of everything from crude petroleum to a bar of highly refined special alloy steel. Both the apparatus and the methods to be used in testing cement, rubber, copper, non-ferrous alloys, materials of construction, asphalts, road materials, thermometers, etc., come in for their own groups of specifications. One can almost say that nothing can be purchased on the open market without its having been tested some time during its production.

Simplification and Standardization of Testing Apparatus

As a result of the work of these various technical associations has come a realization of the danger of duplication by

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[1] Received March 2, 1929.

[2] National Research Council, *Bull.* 2.

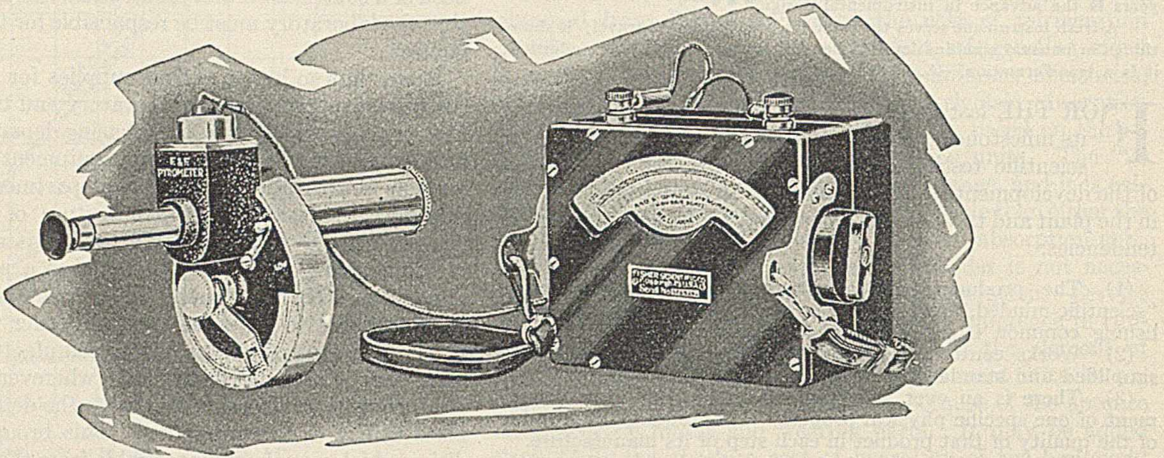
[3] *Ibid.*, *Bull.* 60.

[4] Bur. Standards, *Misc. Pub.* 90.

[5] A. S. T. M. Year Book, August, 1928.

[6] A. S. T. M. Tentative Standards, 1928.

various manufacturers or technical organizations, and consequently an attempt is being made to simplify and standardize the method of test and the specification for the apparatus to be used. This can be amply illustrated by a reference to such a simple instrument as a thermometer. Commercial testing laboratories were required to have 150 to 200 different types of thermometers in order to be equipped for testing the average run of technical products. Today only about 30 different types are required. About five years ago there were over 40 control types of gas apparatus on the market, which types were considered more or less acceptable and standard. A study of these soon showed that there was a needless duplication of equipment, all designed to accomplish the same ultimate results. This meant that a manufacturer would have to carry in stock all parts for the 40 types of gas apparatus and be ready to supply replace units at a moment's notice. As a result of standardization and simplification a complete gas-analyzing apparatus for almost any gas can be assembled in about five minutes from standard parts carried on the shelves of the manufacturers.



F. & F. Pyrometer
A standard direct-reading pyrometer for the high-temperature range

Work of A. C. S. Committee on Standardization

The Committee on Standardization of the American Chemical Society, coöperating with the Scientific Apparatus Makers, found 126 different kinds of laboratory burners. It also found that different manufacturers made the supposedly same style of burner, bearing the same name, with different proportions, such as height, size of gas connection, diameter of tube, etc. By considering as different burners only those that differed in controlling specifications, there were 230 different laboratory burners.

The American Chemical Society's committee could find no need for this array of different burners, nor could it discover any reason for the existence of the majority of them, other than the fact that it had been the practice, first abroad, then in this country, for each decade to conserve the burners inherited from the last decade and to add a few more. As a result of this standardization work the retention of only 32 burners was recommended. These have since fulfilled all the requirements of laboratory work.

The item of burners is only one which was simplified and standardized by this committee. Others are still under consideration. As a result, the appliances retained have been improved, manufactured in larger quantities, and their prices materially reduced.

A Single Control Instrument for Each Test

With the enormous increase in specifications for products, and the consequent increase in time consumed in testing, the producer has reduced the testing of products to an absolute minimum. This has led to the development of highly specialized testing apparatus. There is an increasing utilization of the measurement of one specific property of a substance involved in production, as a test of the quality of the product. This has invariably meant the development of an instrument designed to measure only one property of a substance and do this in a minimum of time and in the most convenient manner. Where once analyses of products required several days, today the entire output of a plant can be controlled by a single instrument involving very little technical skill and requiring only a few minutes for a complete test. Wherever possible the test itself is made automatically. This is probably one of the most outstanding developments in the laboratory and works control apparatus in the last generation. Some of these are cited below.

Manufacturers Coöperating with Users of Instruments

Another factor in the development of works control and laboratory testing apparatus is the new attitude of coöperation between the manufacturers and users of testing equipment. Fifteen years ago the criticism was made, and with some justification, that the American scientific instrument and chemical reagent industries were indifferent to the sporadic and odd needs of research, particularly those which required considerable extra time for the development of equipment and involving insignificant sums of money. Today all the leading concerns in both fields are continually developing new products to meet specific needs. Their desire to develop new and better products is just as sincere as their endeavors to find greater applications of old products. A few years ago the laboratory apparatus industry relied for its consumption upon the activities of salesmen and an excessively heavy advertising budget. Today we see, instead of the salesmen, entire forces of technically trained men, each one a specialist in his own line, ever ready to meet the customer in his own works and help him solve his problem as it arises. We know of one company which employs technical graduates, and which expects each one in its service department to be able to act as a technical adviser, not only in questions of apparatus, but also in methods of use. What is being done in the laboratory supply industry is being done in the works control industry in general.

Control Instruments

A discussion of this type would not be complete without a reference to some of the fine instruments recently developed. Obviously all cannot be described. Those which have been chosen are typical of their field, and are grouped according to the function they perform as control instruments.

COLORIMETERS—Colorimetric analysis, color analysis, and color fading have recently been receiving much emphasis. Among the colorimeters[7] in prominence today from a works control viewpoint are: (1) the liquid depth colorimeters like the Kennicott-Campbell-Hurley, the biological type made by Bausch and Lomb and Spencer Lens Company, the Saybolt, the Robinson, etc.; (2) the standard glass type like the Lovibond and Union. These are all essentially color comparators, in which the unknown color is matched against an arbitrary standard. The tendency is to employ glass standards wherever possible, so as to minimize possible error due to fading of the standards.

The color analyzers being used today are the Ives tintphotometer with its primary glass standards, the Eastman Universal colorimeter, and the Harvey automatic spectroanalyzer, which employs a light sensitive cell. Each has its field and own set of followers. Each machine has its advantages, but limited production has restricted their use somewhat in routine laboratories. The degree of blackness or grayness of a cloth or pigment can be determined either alone or in conjunction with an undertone of one of the primary colors in the Ives and Eastman instruments, while grayness can now be indexed on the Johnson nigrometer.[8] This late arrival has already established itself in the paint, enamel, ink, and carbon black industries. Sheen, which has so often interfered with color analysis, is now being recognized as a separate property of materials and is being measured and studied on the Ingersoll glarimeter.[9] Cloth, silks, crystals, celluloids, paints, enamels, and glasses are all being controlled by means of these instruments. New instruments are still needed to solve color differences which can now be detected by the eye, but for which there is at present no measuring instrument. Perhaps, when the fundamental principles of colorimetry are better understood, such instruments will be forthcoming.

The fastness of dyes on clothing, silks, tapestries, and even the color of glasses and enamels are being controlled and still studied through the use of the ultra-violet and arc lamps. Rubber is now artificially aged with these, so as to foretell its probable length of life.

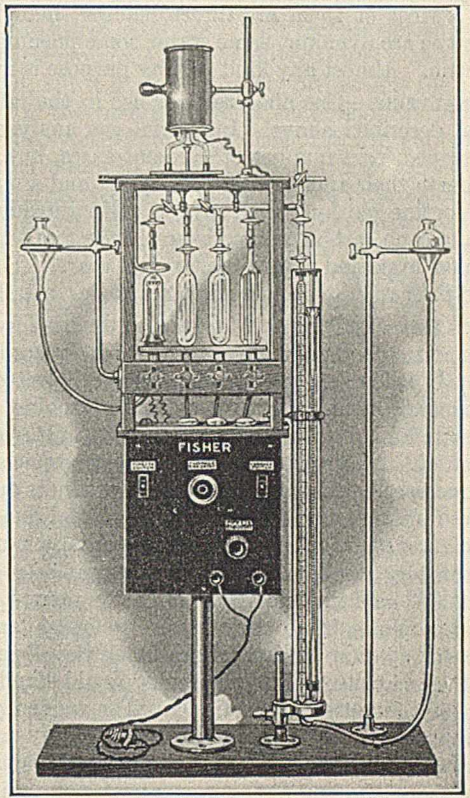
HUMIDITY CONTROLLERS—Industrial humidity controllers have been available for some time. Several companies are now in the field. Their machines have come to stay. Very recently a small laboratory-size humidifier and indicator has appeared. It is so new one can hardly foretell its many uses. The paper, paint, textile, clay, and lacquer industries rely upon it as the governor of their rates of production.

HEAT INDICATORS AND CONTROLLERS—In plant control heat measurements have finally settled to a definite, reliable basis. The thermocouple still holds the field for wide-range, long-distance indicating and recording instruments. An interesting development has been the harnessing of the feeble current generated in a thermocouple to warn the operator, by lights, bells, or other signals, of the conditions of the unit at all times and to control, through relays, an entire plant. Most of the instruments on the market are direct reading, very reliable, and reasonably cheap both as to initial cost and routine upkeep. The old stand-by, the platinum resistance thermocouple, still maintains its former prestige as reference standard, but is rapidly being displaced by the base-metal thermocouple for control purposes. Standard samples of tin, zinc, aluminum, copper, etc., with known melting points are now obtainable from the U. S. Bureau of Standards. These are recommended as standards for the calibration of thermometers and pyrometers.

The vapor pressure type of pyrometer is rapidly invading the field of the thermocouple pyrometer, but because of its nature is somewhat restricted in its range. New models of radiation pyrometers are always appearing. Their tendency to give false readings, when used by inexperienced operators, has brought this type into some disrepute. However, education of the user by the manufacturer is gradually improving conditions.

Optical pyrometers of the disappearing-filament type occupy the predominant position for the higher ranges of temperature and have been accepted as standards. One of these is direct reading. Their one drawback, that of requiring black body radiation conditions for optimun accuracy, still limits their usefulness in some respects. Manufacturers realizing this have issued tables of corrections to be applied to take care of the various conditions obtaining in works control. But for duplicating satisfactory results the use of the correction table can be eliminated.

Pyrometer upkeep has developed a pyrometer engineer—a man solely responsible for maintainence, accuracy, and calibration. Most manufacturers are employing trained men in their service departments, and distribution centers throughout the country.



Fisher Universal Gas Analyzer

Thermometers have become pretty well standardized within the last few years. Thirty years ago almost any calibrated glass tube containing an expanding liquid was considered satisfactory. About twenty years ago the fundamental principles underlying thermometry began to be studied and thermometer manufacture was reformed. Theory rather than use was emphasized and specifications for thermometers were made by the thousands. Specifications became so numerous that, while fulfilling some, others just had to be ignored if

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[7] Snell, "Colorimetric Analysis," p. 2, D. Van Nostrand Co., New York, 1921.

[8] *The Laboratory*, **2**, 21 (1929); Johnson, *Paint, Oil Chem. Rev.*, **86**, 14 (1928).

[9] Ingersoll, *Paper Ind.*, **2** (1921); Harrison, *J. Am. Ceram. Soc.*, **49** (1927).

commercial production were to be considered. Meanwhile the number of thermometers specified increased by leaps and bounds. Conditions became so bad that manufacturers became desperate.

Thanks to the coöperation between the American Society for Testing Materials,[10] the International Congress for Testing Materials,[11] the Bureau of Standards,[12] and some of the manufacturers, the theoretical aspects have been viewed in the light of manufacturing difficulties and reliable thermometers have evolved. This evolution is still continuing. Specifications are still being made as necessary, but the number of thermometers being specified is gradually growing smaller and smaller.

There has been one very interesting recent development in thermometers. A quartz thermometer,[13] filled with gallium or a mercury alloy, for use up to about 1000° C., has been developed by the General Electric Company, although as yet it is not being produced commercially. This fills the gap between the cheaper glass thermometers for low temperature range and the more expensive thermocouple and optical pyrometers for the higher ranges. There is yet, however, a definite need for a cheap, accurate, rugged temperature indicator covering a range of about 500° C. up, which would not have the disadvantages of the present types.

LIQUID AND GAS METERS—In liquid measurement we have seen many new instruments developed. Liquid depth, velocity, capacity, pressure, and density meters are appearing in numbers. Most of them are direct reading, many are recording, some are dynamic, some static, some pneumatic, and some electric. Almost any kind for any purpose is available.

GAS ANALYZERS—Gas analyzers for use in the laboratory have been described above. Industrial gas analyzers have been developed for a number of different gases, but are as a rule specific in their application. Analyzers and a number of recorders for flue gas, hydrogen, oxygen, sulfur dioxide, carbon dioxide, and even carbon monoxide are on the market. Most of these have appeared within the last few years. They have all proved their worth within a short time after installation.

ACIDITY AND ALKALINITY METERS—Industrial hydrogen-ion concentration and conductivity meters and recorders have only recently come into prominence. Paper, electroplating, sewage disposal, water purification, leather tanning, textiles, and foods are all being studied with a view to ultimate automatic control. Many installations are in service. Aside from the increased value of more uniform products due to the use of these instruments, the saving of material due to their installation has paid for their original cost many times over.

For laboratory steel analysis the hydrogen-electrode titration outfits still hold the field against all newcomers. In other analyses the quinhydrone electrode is preferred, and other electrodes for specific conditions are being developed daily. Colorimetric pH comparators employing liquid standards are available for the entire range of pH. The tendency of the standards to fade, particularly in the strongly acid and strongly alkaline ranges, had led to the gradual displacement of this type by one employing permanent non-fading glass standards. Convenient portable outfits in both types are available in all ranges.

VISCOMETERS—For viscosity control the Saybolt viscometer for lower ranges and the Furol for slightly higher ranges still are paramount. These can now be obtained in automatic models. For viscous materials like lacquers, paints, rubber cements, the Gardner-Holt mobilometer[14] is being rapidly recognized as a handy control unit. Plasticity measuring machines have appeared, but their use is still somewhat limited.

SCALES AND BALANCES—Uniformity of product always depends upon the relative weights of the ingredients. Time- and labor-saving scales are being developed continuously. There are now available automatic recording weighing machines which, to satisfy the fastidious, even have automatic samplers attached. All industrial sizes are available. In the field of little things a new keyboard analytical balance, which looks somewhat like a typewriter, has made its appearance. This is a real time saver for control weighings differing from each other by fractions of a gram. For still finer weighings a micro-balance weighing to 0.001 mg. is in daily use in several laboratories.

Two outstanding developments of last year were the Knowles glow tube, and Wensley's Robot.[15] By changing the capacity of a Knowles tube, which looks like an overgrown radio bulb, relays are activated and limitless power can be controlled. In a recent demonstration a man waving his hand over the bulb in his office in the East started an all-electric rolling mill in Homestead, Pa. This same type of bulb controls the moisture content of paper. The Robot, based essentially on tuned radio circuits, responds to a sound of definite pitch and controls through relays processes miles from the source of the sound. These are as yet in the experimental stage, but who would dare predict what technical process could not be controlled by these almost human machines.

Laboratory Glassware, Porcelain, and Chemicals

In discussing control and laboratory apparatus, one cannot help but think of laboratory glassware and the chemicals which go to make up the bulk of the every-day supplies of the chemist. In the perfection of these, great strides have been made. Foreign glassware, both graduated and ungraduated, was considered the best until about 1914. Domestic production, suffering from lack of protection, was sadly discouraged and production limited to a very few lines. When thrown on its own resources, America just had to produce its own laboratory equipment or the very field equipment of our armed forces, which depended on this for its production and control, could not have been produced. Scientific education and public health activities could not have been continued. This sudden shortage proved a blessing in disguise.

Glassware was the first to require immediate attention. While the first produced in this country was not all we might have desired of it, it did tide us over until we could work out the details. Today we have a laboratory glassware industry, producing a chemical- and heat-resistant glass that compares very favorably with the best foreign ware. Graduated glassware, burets, cylinders, pipets, etc., are now made with the aid of new dividing and engraving machines, with a uniformity and accuracy never equaled abroad. Chemical porcelain ware, one of the very difficult products for Americans to develop because of relatively no experience in this line of production, has come through with high chemical, heat, and mechanical shock resistance, wonderful uniformity of size and shape, and is now reaching a large-scale production basis.

Before the World War Germany was the only producer of special chemicals. Today one manufacturer alone makes 2450 different organic chemical reagents, hardly any one of which can be considered as having reached the commercial production stage, but each one virtually essential to chemical research or control in one phase or another. Another manufacturer has put out a complete line of analyzed chemical reagents, of a degree of chemical purity on a par with the best

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[10] A. S. T. M. Standards, 1927, Part II, p. 996.

[11] Intern. Cong. Testing Materials, 1927, Part II, p. 689.

[12] Bur. Standards, *Circ.* 8 and 66.

[13] Berry, *Trans. Illum. Eng. Soc. (N. Y.)*, 21, 552 (1926).

[14] *The Laboratory*, 1, 36 (1928).

[15] Free, *World's Work*, February, 1929, p. 47.

foreign makes. Other houses are developing similar lines. Much has been already accomplished—much still remains to be done.

Prices have on the average been reduced about 25 per cent on organic and about 20 per cent on inorganic chemicals. Porcelain itself experienced a 40 per cent reduction not very long ago. The entire line of laboratory equipment, in spite of the many improvements, is now about 18 per cent cheaper than in 1920.

Conclusion

As new products are put on the market, the manufacturer is continually faced with the problem of finding means whereby those products can be controlled and tested. New methods must be devised and frequently new materials developed. In all this, the manufacturer of such testing equipment is in a position to render real service. He develops the instruments which stand guard over the traffic of materials through a plant and mean profit or loss to an industry.

One of the most encouraging signs of the advancement and application of science in America is the fact that the American scientific instrument industry is no longer a matter of mere merchandising, but is now the performance of a vital function—the design, manufacture, and supply of the proper scientific tools with which the scientist can obtain the particular result he desires.

Chemical Prices React to Technical Advances[1]

Williams Haynes

Chemical Markets, 25 Spruce St., New York, N. Y.

CHEMICAL market prices fluctuate, as the saying is, "high, wide, and handsome." There is a reasonable explanation for this economic phenomenon, since the function of price is to maintain a balance between supply and demand, and in the chemical markets one of these elements is quite inflexible.

The gluts of overproduction are cured by falling prices, which tend to check productive activity, and at the same time stimulate greater purchases. Contrariwise, higher prices, in a time of goods famine, encourage production and discourage consumption. Plainly, if consumption is but little affected by price, the burden of adjusting supply to this staple demand will fall upon the producers themselves, and it follows naturally that price fluctuations will be much more frequent and more severe.

Although these conditions obtain in the field of chemical price making, and indeed constitute one of the chief and basic hazards of any chemical enterprise, nevertheless there are longer periods over which broader, more significant price trends may be traced. These general movements of chemical prices arise from fundamental conditions. Usually their origins are far removed from the direct influence of the chemical industry, such as the general decline in all price levels in the period between our Civil and our Spanish wars or the sharp up-swing of all prices during the World War, but there is one highly effective factor in chemical price making that is wholly chemical. It lies, in fact, in the hands of the chemist and the chemical engineer. It is technical advance which, as William M. Rand has pointed out, is the cause of most of the truly revolutionary chemical price changes.

Today new developments in chemical manufacturing technic dominate the trend of chemical prices. In 1920, when the bubble of the post-war price inflation burst, there was initiated a painful period of price deflation. Mercifully this critical stage was not of too long duration. Though aggravated by a serious overproduction (built up during the war), it was generally past by 1924. But the trend of chemical prices has continued downward. Long after deflation proper is finished, after the worst of our overproduction has been cured, technical advances are having their direct economic effect, not only in opening up new markets, but also in lowering the cost of important groups of chemical raw materials for a score of important industries.

It could hardly be otherwise. The decade since the close of the World War has been marked by an astonishing industrial development in chemical fields. Synthetic nitrogen has won control of the world's market. More than this, it has introduced into commercial practice an entirely new chemical engineering technic, that of gases in reaction under high pressures under carefully controlled temperatures with or without the use of catalysts. This technic not only has given us synthetic ammonia, and as direct result a new process for nitric acid, but it is also indirectly responsible for a synthetic process for the manufacture of methanol; it promises the commercial synthesis of ethyl alcohol, the larger employment of the rich chemical stores in natural gas, new methods of manufacturing acetic acid and its allied products, and has already opened up new commercial opportunities for hydrogen, chlorine, and a score of other chemical products.

The Brewster process for the direct recovery of acetic acid from wood distillation liquors, improved technic in the handling of the brines at Searles Lake, Calif., new catalysts for the sulfuric acid contact process, and marked improvement in the methods of producing and handling esters are but four of a number of widely different strictly chemical developments that have had far-reaching commercial effects. Phenol, phthalic anhydride, aniline oil, phosphoric acid, and acetic anhydride are all being manufactured today by new, improved processes which have directed prices downward.

In quite another direction technical advance has affected chemical quotations. The whole of the artificial fiber and the cellulose plastic lacquer industries have been built up during the past decade. They have created tremendous new chemical demands. The growth of the automobile industry has resulted in a bewildering expansion of the market for so-called artificial leather and for tires, the latter in turn being responsible for the notable advances in the field of chemical accelerators. Chromium plating, radio, and color photography have created new chemical industries selling new chemical products in new markets to new consumers.

Even to record a bare list of the technical developments of commercial importance during recent years would trespass over the limits of this paper—indeed, this whole issue of Industrial and Engineering Chemistry is devoted to such a review of progress—and there are few of these which have not had their repercussions upon chemical price quotations. Without doubt these technical developments are the dominating influence upon chemical markets today, and it is fairly obvious that this technical era is still only in its beginnings. I dare to prophesy—in full knowledge of the dangers that lurk in any system of price forecasting—that unless some unfore-

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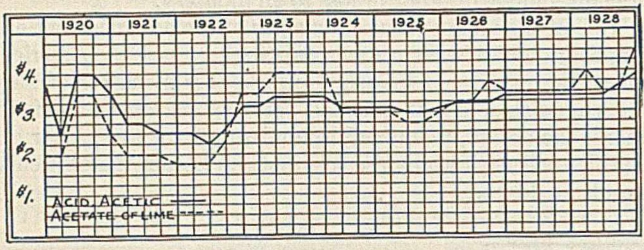
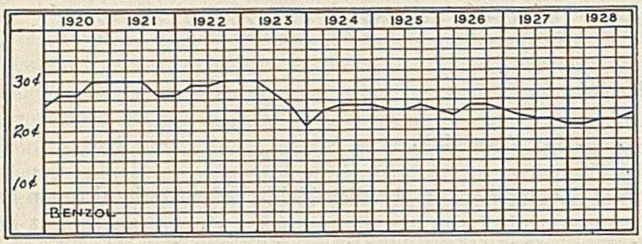
[1] Received March 26, 1929.

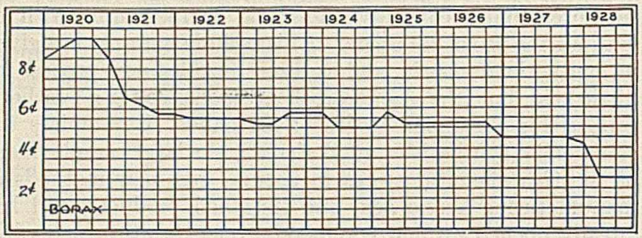
seen factor disturbs the basic economic situation, chemical prices during the decade to come will continue to decline, and that the impetus of this downward price movement will be furnished by the successful results of extended chemical research in industrial fields.



Acetic Acid and Acetate of Lime



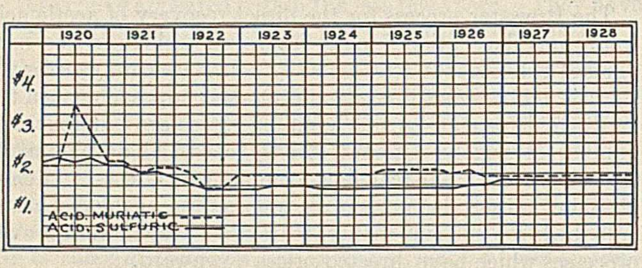
Benzene



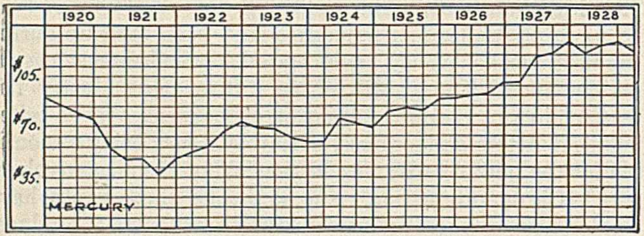
Borax

Knowledge of such a basic trend in chemical prices is full of important implications. The switches and swings in the quotations of any individual chemical item are full of fascinating interest. They have a historic value, and they are of gravest concern to those who produce, or handle, or consume that particular chemical.

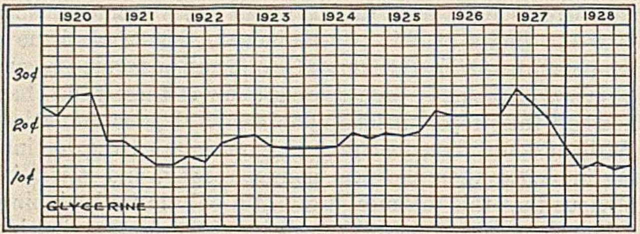
The market for mercury, for example, is today the result of a bitter fight for control between the dealers in London and the producers in Spain and Italy, a battle which paradoxically has raised the price to a point where it is feasible for American mines, whose costs are high, to produce. To understand this situation it is necessary to know that the biggest and most economical producer is the Almaden mine owned by the Spanish government. This output, until 1922, was marketed by the Rothschild syndicate, which bought the output until the Spanish government canceled their old agreement and began open selling to the highest bidder. This turned the entire market over to unscrupulous speculators, so two years ago the government sold its output to a new syndicate controlled by a small group of London dealers. The quantity to be bought was specified in the contract, but the buyer was given an option at the same price on all excess production. Because the London group was able to make exorbitant profits, the contract was not renewed this year, but the Spaniards entered into an agreement with the three Italian mines, controlled by the government bank in Rome, to market directly all their own quicksilver during 1929. Having a large stock available and being strongly backed financially, the English syndicate determined to make the path of the new direct-selling organization as rocky as possible by means of iron-bound contracts with consumers around the world and by running the price as high as possible in order to create all the possible buying resistance. The mines have cut the price sharply, but it is still sufficiently high to allow a reasonable margin of profit to the half dozen small American mines, which have been producing



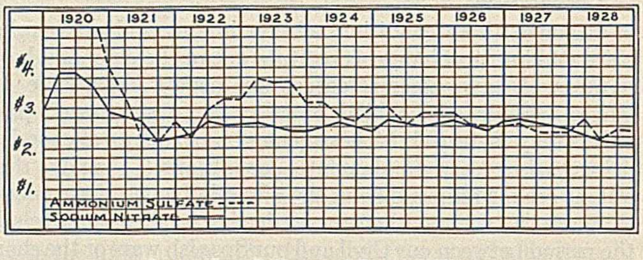
Sulfuric and Muriatic Acids



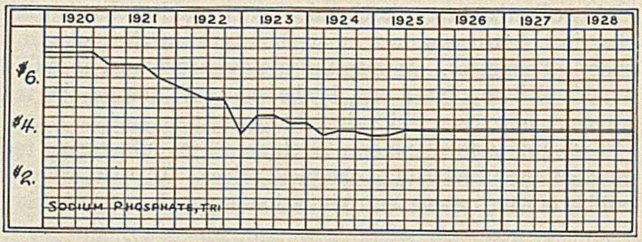
Mercury



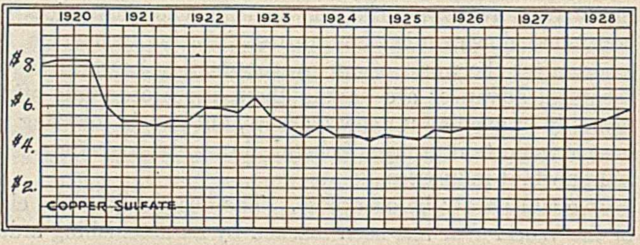
Glycerol



Ammonium Sulfate and Sodium Nitrate



Trisodium Phosphate



Copper Sulfate

in sufficient quantities to have an appreciable effect upon our domestic market.

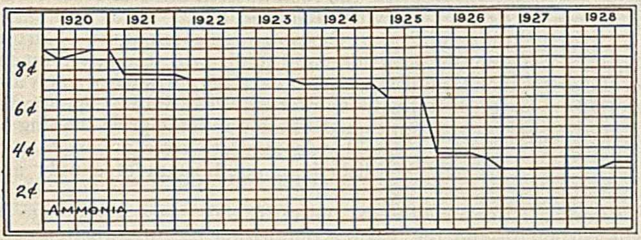
While all chemical prices are not quite so romantic as this mercury situation, still each quotation is the result of the interplay of direct influences. Although these influences often touch several different chemical products, nevertheless any one is always an individual case. They are isolated and rapidly changing examples of the practical economics of price making, but of little value to any save those intimately concerned. Not so, however, with the influences that control the broader price trends.

Appreciation of the control which technical advancements will exercise over chemical price movements in the immediate future has wide application. To the chemical manufacturer it means that the destiny of his business lies in the research laboratory. The same lesson is plain to the forward-looking executive in any industry employing chemical raw materials in chemical processes. For the banker a plant without a good laboratory becomes thus a "poor risk." For the chemist and the chemical engineer this commercial importance of research holds a golden opportunity. An academic acquiescence in the fundamental importance of research on the part of executives and financiers is one thing. It is quite a different thing for them to be able to translate technical developments directly and promptly into the terms of profit and loss, success of their enterprise or its failure.

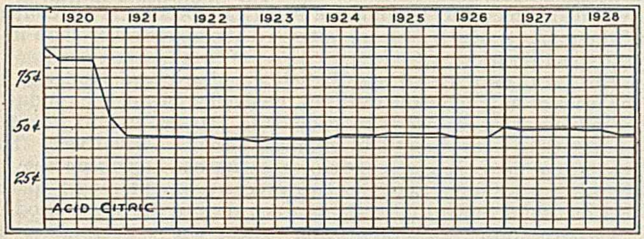
Price Charts[2]

ACETIC ACID AND ACETATE OF LIME—The bulk of our acetic acid is produced from the acetate, but the historic relationship of the two prices has been upset by the increasing output of acid produced direct from crude wood liquors and by the synthetic production since last summer at Niagara Falls. Without these and greatly increased output in the South, the rapidly growing demands of the solvent and rayon industries would have run the price even higher.

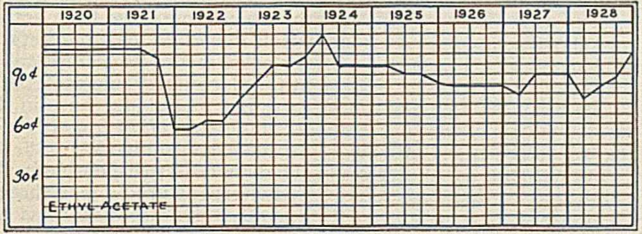
BENZENE—Our tremendous expansion of benzene production during the war period has been taken up by the motor fuel blenders, who now take in 80 per cent of our 12 to 15 million gallon output. Since 1924 the growing use of toluene by the lacquer industry has tended to stiffen the benzene market, which is now governed by steel industry activity for supply and the gasoline price for demand.



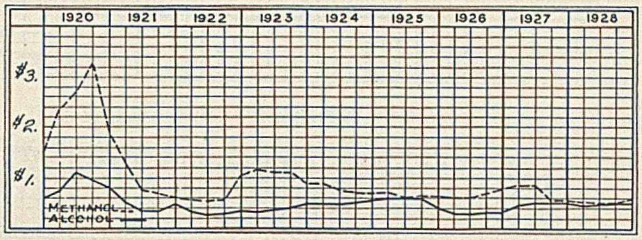
Ammonia



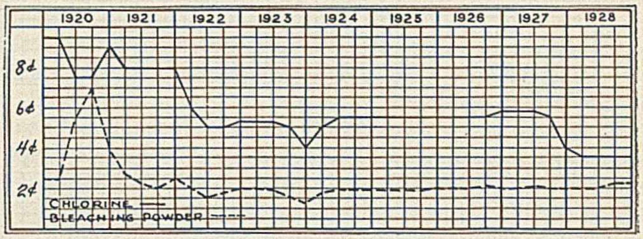
Citric Acid



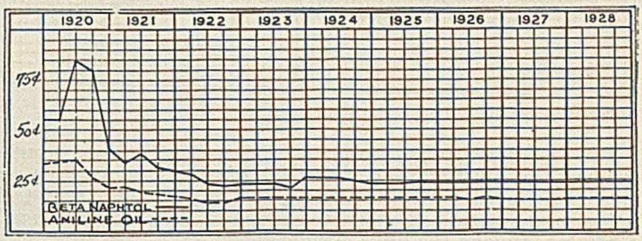
Ethyl Acetate



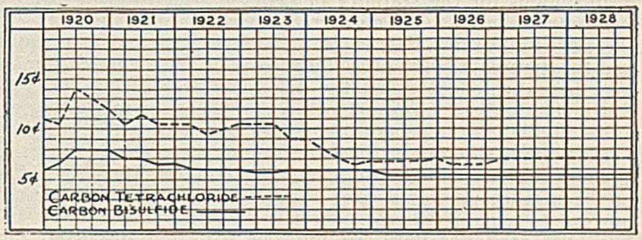
Methanol and Alcohol



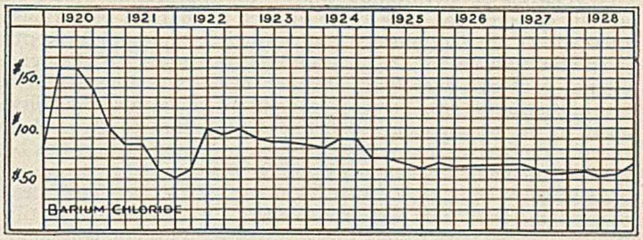
Chlorine and Bleaching Powder



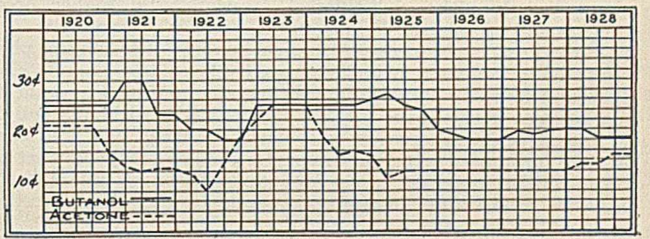
Beta-Naphthol and Aniline Oil



Carbon Bisulfide and Carbon Tetrachloride



Barium Chloride



Butanol and Acetone

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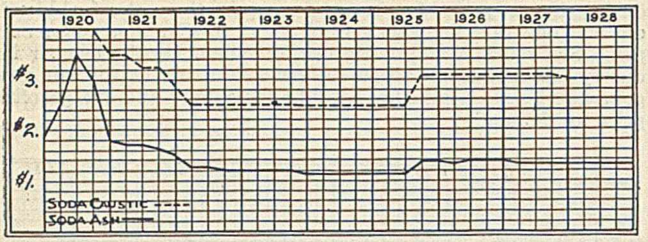
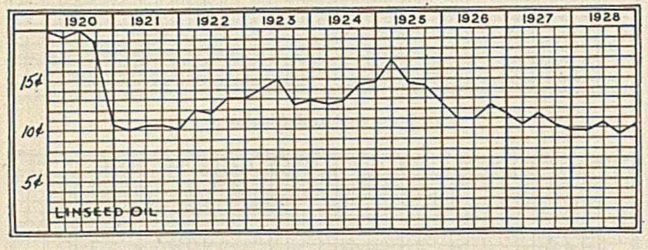
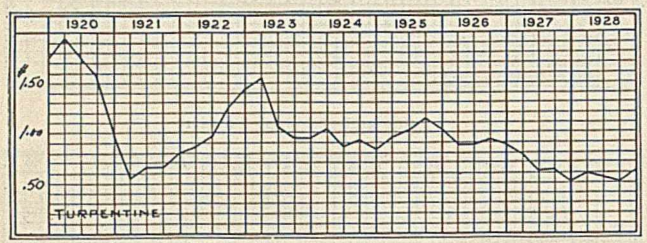
[2] Price charts plotted by Elmer F. Sheets.



Caustic Soda and Soda Ash



Linseed Oil



Turpentine

Borax—Borax prices stand today at virtually 25 per cent of the post-war inflation peak and at half of what has long been considered the normal price level—a direct result of improved technology and determined efforts to expand the market for this mild alkali by bringing the price down.

Sulfuric and Muriatic Acids—The mineral acids have long been famous for the stability of demand which during the past two years has resulted in a generally firm and quiet market. But there are indications of changes. Muriatic is increasing in supply and the manufacture of nitric by the direct oxidation of ammonia may be expected to upset the price equilibrium in this group. Better methods of transport will widen the sales marketing area and will disturb the geography of the industry.

Mercury—Mercury prices represent the fight between the London dealers and the producers in Spain and Italy for control of the market—a commercial battle which has carried the price upward to a point where American high-cost mines have been brought into operation—an unusual situation discussed more fully in the text.

Glycerol—A by-product and with appreciable stocks imported, glycerol has long been subject to marked variations in price which have doubtless contributed to the cordial reception given by consumers to glycerol substitutes. While glycol has not captured the dynamite market, as was forecast, it has cut appreciably into glycerol consumption, as also has invert sugar in the pharmaceutical field. The failure of glycerol producers to move big tonnages into the antifreeze market has been the final element of weakness in glycerol prices.

Ammonium Sulfate and Sodium Nitrate—The period covered by the chart saw the control of nitrogenous fertilizer material prices pass from Chile nitrates to synthetic compounds, although the sulfate, being a by-product, must always be absorbed whatever the price Of late sulfate has been firm and nitrate weak, although stiffened somewhat by higher ocean freights and promises of help from the Chilean government.

Trisodium Phosphate—Although imports of trisodium phosphate have increased from 5 to nearly 20 million pounds since 1925 and two new large producers have come into the domestic market, nevertheless the market has held firm, although subject to considerable undercover price-cutting during 1927 and early in 1928, prompted largely by importers. The prospects that the tariff will be increased more adequately to offset differences in American and European production costs are considered excellent in Washington.

Copper Sulfate—Prices of this chemical, which is finding an expanding market as a soil conditioner and insecticide, are predicated directly upon price of the metal, and the continued rise of copper during 1928 and the first quarter of 1929 is reflected in the advancing price of the salt, following a lean period when there were very heavy imports from Germany.

Ammonia—Aqua ammonia prices tell the story of the invasion of this market by synthetic material, the sharp cut during the fall of 1925 being a tardy attempt on the part of sellers of by-product material from the gas and coke industries to check this onslaught. After two years of extreme weakness ammonia prices have stiffened markedly owing to increased use in the fertilizer industry and in nitric acid manufacture by direct oxidation, a tendency toward higher prices which even the increased production from Hopewell has not checked.

Citric Acid—For the past couple of years the domestic producers have ruled the market and the recent announcement of an improved process of manufacture promises but the more firmly to establish domestic control—a pretty example of the stabilizing effect upon the price of what has traditionally been a highly speculative item.

Ethyl Acetate—The rise in ethyl acetate prices during the years 1922–23 reflects the insistent demands of the rapidly expanding lacquer and rayon industries. Its decline since then has been under the influence of a flood of imported acetates. Its recent upward turn is due to obscure market influences associated with periodical shortages of potassium hydroxide in the New York market.

Methanol and Alcohol—The drop in methanol prices in 1924 represents the arrival of German synthetic material—an invasion stopped by the President's tariff action—while the dip during the last half of 1927 tells of the first domestic synthetic production. While alcohol prices have been maintained at steady levels during the past two years, the elimination of price slashing through mergers and the Doran limitation of output has greatly improved the general tone of the market.

Chlorine and Bleaching Powder—Since 1923 the production positions of chlorine have been almost completely and directly reversed; chlorine has jumped from 62,000 tons to close to 200,000 tons, while bleaching powder has fallen from 150,000 to 55,000 tons. Chlorine prices have come down and down in response to increased production, and although there has been a tremendous increase in consumption the marketing problem is still perplexing.

Beta-Naphthol and Aniline Oil—These important intermediates furnish splendid examples of the tremendous strain of deflation which the coal-tar chemicals, including the dyes and the pharmaceuticals. went through in the post-war period and the measure of stabilization on the rock-bottom basis of costs which this branch of the industry has achieved.

Carbon Bisulfide and Carbon Tetrachloride—Carbon bisulfide consumption has gone up rapidly with the development of the artificial silk industry, so that even the entrance of a new and aggressive producer into the market last year did not openly disturb the price quotation, though there was some price shading on big contracts. The tetrachloride market, after a bad case of overproduction, has established an equilibrium of supply and demand.

Barium Chloride—Since the tariff was raised a year ago on the carbonate and the Tariff Commission has investigated comparative costs of production on the chloride, this material has continually stiffened in its market position and imports have dwindled somewhat, leaving the American producers in control of the market, which appears to be in a strategic rather than in a statistical position.

Butanol and Acetone—The steady downward tendency in the price of butanol is the result of the fixed policy of the producer to reduce prices in order to widen the market and to forestall competition, both direct and indirect, through derivatives. The constantly increasing strength of acetone has suggested the interesting possibility that the two products might revert to the relative importance that was obtained during the war period.

Caustic Soda and Soda Ash—After the proverbial seven years of weakness, the market position of these most important of all alkalies has become very firm since the revival of general industrial activity a year and a half ago. There have been even brief periods during recent months when there have been actual spot shortages of these basic materials in certain local markets.

Linseed Oil—Last year witnessed a record consumption of linseed oil, in defiance of the threat that lacquers would materially cut its use in paints; and unless there is a marked advance in the tariff (which is likely) there appear to be no market factors tending to higher prices in this highly speculative commodity.

Turpentine—Any decline in the demand for turpentine in the paint industry has been offset by new terpene products, although the improved technology of the naval stores producers has enabled them to increase their production and improve their quality.

Mechanical Handling of Materials in and about the Chemical Plant—I[1]

A. K. Burditt and W. F. Schaphorst

45 Academy St., Newark, N. J.

WHAT is the most economical mechanical handling method for us to use? This question is commonly asked by officials of chemical concerns. Chemical plants are among the foremost users of mechanical handling; yet information on the subject as applied to these plants is particularly scarce.

In searching for data we have found that as a rule manufacturers of material-handling equipment are more willing to assist with data than are the chemical institutions themselves. The feeling seems to prevail with many manufacturers, not alone in the chemical industry, that when the most economical method of manufacture is attained facts pertaining to it should not be given to the world lest competitors take advantage of it.

Facts in abundance are already available on the general problems of handling materials, all of which are applicable to the handling of many materials used by chemical companies. For example, adequate data covering speeds of operation, carrying capacity, power requirements, and operating costs covering several types of conveyor systems for handling various solids in bulk form have been prepared by Trautschold.[2]

The present article will attempt only to show representative types of equipment for handling solid materials in bulk as well as in containers, and briefly to describe their operation. Based on this preliminary background, subsequent articles will go into more detail in analyzing the application of each type of equipment in representative chemical plants.

It is difficult to make a systematic analysis of material-handling equipment in the chemical field because this field is so diverse in character and, therefore, in requirements. No one type of equipment can be considered as the "one best way" of handling a certain material in a certain form. There are so many factors involved that what is true for one plant may not hold true for another.

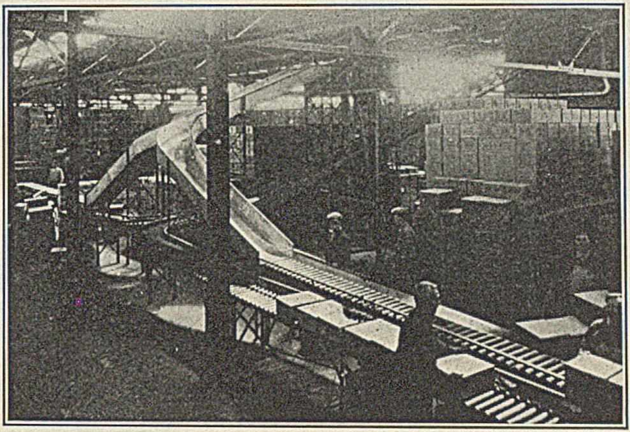

Courtesy Standard Conveyor Co.

Figure 1—Handling Cartons on Chutes and Gravity Rollers

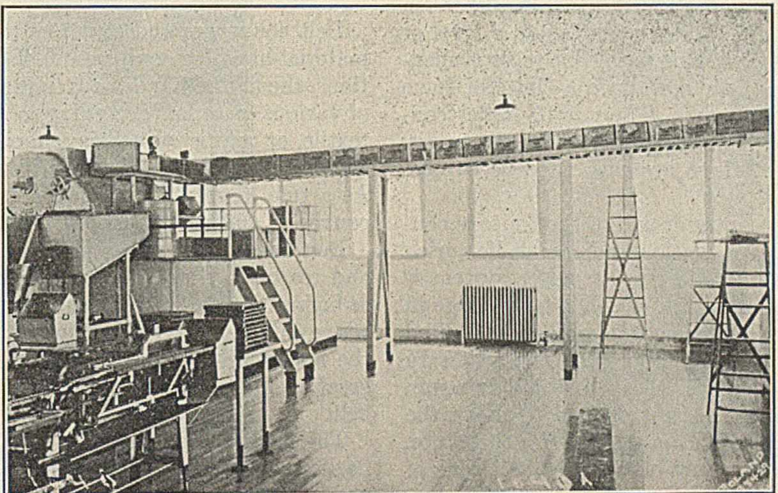

Courtesy Standard Conveyor Co.

Figure 2—Overhead Gravity Roller System for Cartons

The broad back of the day laborer was the original means for handling solid and even liquid materials. The principal reason for superseding this means with mechanical handling of materials is the expense and limited capacity of the laborer. So long as horse power is cheaper than man power, competition makes mechanical handling necessary. The problem of the plant operator is not so much whether to adopt mechanical handling of materials as to determine the most economical method of handling after making an analysis of the conditions and requirements of his particular plant.

The applications of mechanical-handling equipment are many, and include the unloading of freight cars or other cargo carriers; the bulk storage of materials; the withdrawal of materials from storage; handling of materials through process; packaging, sacking, or bottling of products; the storage of finished products; and, loading or shipment of products.

Among the types of equipment available to handle the various materials are belt conveyors and elevators; bucket, apron, slat and scraper, or flight conveyors and elevators; spiral or screw conveyors and elevators; gravity roller systems; chutes; pneumatic conveyors and elevators; drag scrapers; skip hoists; and cranes of various types. Most of this equipment can be had in portable as well as in permanent forms.

It is easier to provide for material-handling equipment that is thoroughly efficient in operation in the design of a new building than it is to design a conveyor system to conform to the restrictions of an older building. Production and material handling can be synchronized to best advantage when the building is designed to provide this synchronization.

In adapting material-handling equipment to a plant already in operation, it is necessary to ascertain the required capacity taking into consideration future needs, the space available for the equipment, the distance of portage, the materials to be handled, proper tie-in between different types of equipment, low maintenance cost and dependability, resistance to wear, expense of operation, and convenience. On

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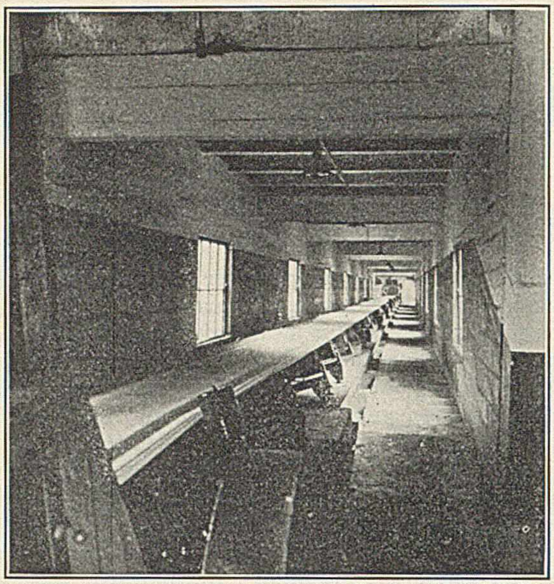
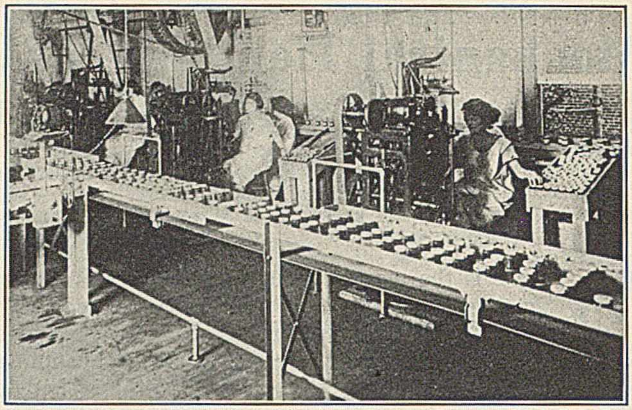
[1] Received March 5, 1929. Other articles in this series will follow in succeeding issues.

[2] See Liddell's "Handbook of Chemical Engineering," Vol. I.



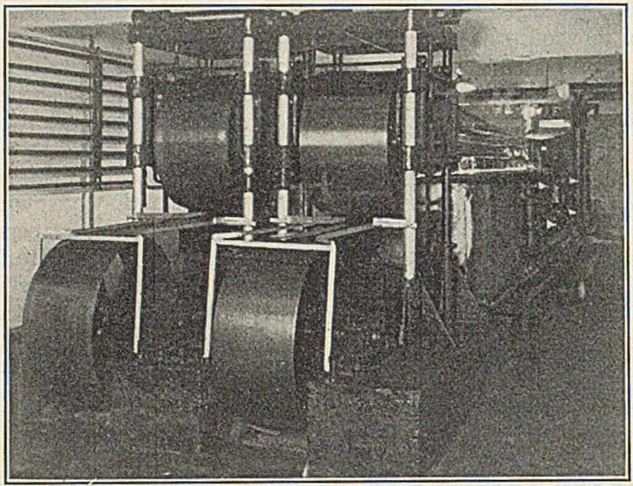
Courtesy Link-Belt Co.

Figure 3—30-Inch Belt Conveyor for Conveying Salt



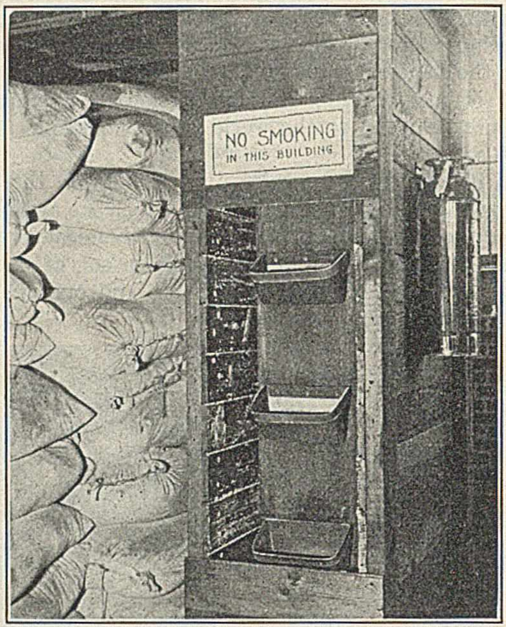
Courtesy Link-Belt Co.

Figure 4—Carrying Small Jars from the Filling Machines



Courtesy International Nickel Co.

Figure 5—Metal Belt Conveyor for "Below-Zero" Operation



Courtesy International Nickel Co.

Figure 6—Elevating Salt on a Belt-Type Bucket Elevator

these factors will depend the choice of the types of equipment that will make up the entire system.

Gravity Systems

When the direction of flow is down, advantage can be taken of gravity in moving material. Movement along a level or the elevating of material requires power. The most elementary system for handling solid materials is a chute of some form or other, requiring no power. The gravity roller conveyor is another type of equipment requiring no power. Figure 1 illustrates both of these systems, the one supplementing the other.

The speed of the gravity conveyor and of the chute is controlled only by the angle of inclination and cannot be varied without changing the angle. The gravity roller system is limited to the handling of containers or solids fairly large in bulk and smooth in surface. The length of portage is limited by the vertical distance available to provide the necessary angle of inclination. The angle of inclination is again governed by the speed at which it is desired to move the material. The same principle, of course, holds for the chute.

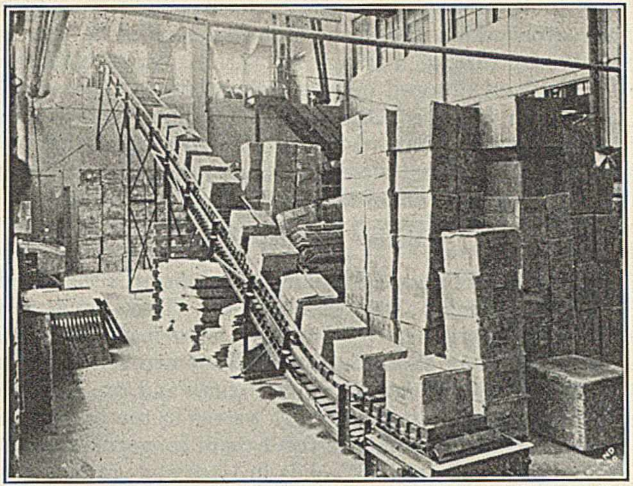
Gravity systems are particularly efficient in buildings of multiple-story construction where the processing or production is begun on the top floor and continued through the lower floors. Figure 2 shows such an application of a gravity conveyor as well as the view shown in Figure 1. Installations such as the one shown in Figure 2 are frequently supported from the ceiling.

Belt Conveyors

Belt conveyors and elevators represent a common type of material-handling equipment. There are two principal variations, the flat belt and the troughed belt. The belting can be of various materials according to its service—leather, rubber, textile, or composition being among the more common types. Even metal belts are frequently used for the flat belt type. As a rule loose materials are carried on the trough type of conveyor, and containers or merchandise on the flat belt type.

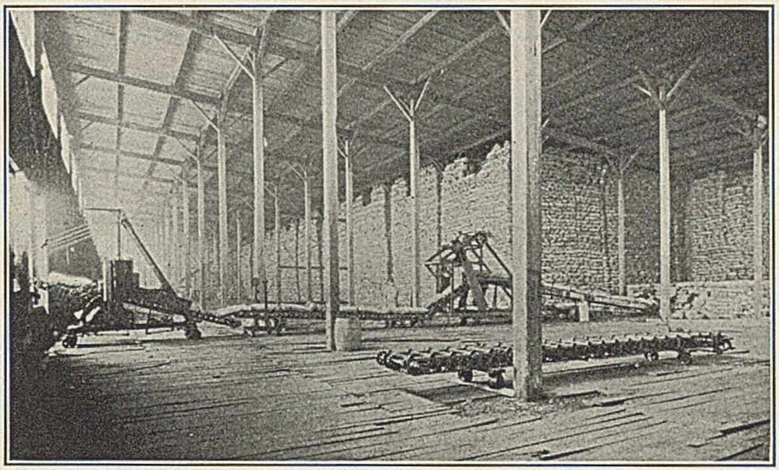
Belt conveyors are especially adapted for heavy capacities and reasonably long hauls. The belt speeds are commonly as high as 200 to 400 feet per minute according to the material conveyed. For elevating materials on the belt conveyor the maximum inclination is usually about 25 degrees. Too great inclination causes slippage and excessive wear on the belt.

The material being handled, in the case of bulk solids, can be discharged over the end of the conveyor, or it can be picked up at any point along the belt and distributed. Belt trippers are frequently used for distributing materials over storage



Courtesy Standard Conveyor Co.

Figure 7—Slat Conveyor System for Elevating Cartons



Courtesy Standard Conveyor Co.

Figure 8—Storage and Reclamation of Sacks of Fertilizer

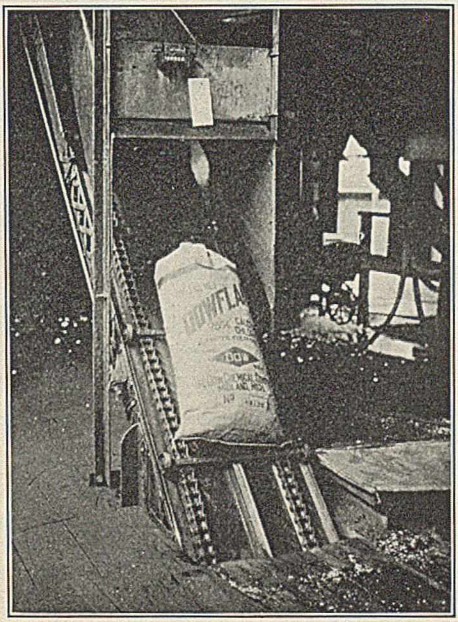
bins, etc. The belt tripper can be moved either by hand or automatically along the belt to pick up the material and to discharge it over the sides of the conveyor. Another common method for discharging material is to pass the belt under a plow that guides the material off the belt at the point desired. A typical example of the troughed type of belt conveyor is shown in Figure 3. This one handles salt. To prevent incrustation and corrosion, all the idlers are granitized. Figure 4 shows an installation of the flat belt type for handling small jars. The jars are brought in single file from the filling machines on a narrow belt and transferred to a wide belt that moves them to the inspection and then to the packing departments. The installation shown in Figure 5 is of the metal belt type. This belt is of monel metal and the conditions under which it operates are unusually severe. The conveyor operates through a temperature 45° F. below zero and is designed to resist corrosion from brine.

Flight Conveyors

The term "flight conveyor" is difficult to define clearly. We have arbitrarily included in this class those types in which a series of carrying units is mounted, ordinarily, on a chain or pair of chains. Apron, chain, scraper, cable, bucket, tray, and slat conveyors are flight conveyors. There are many other varieties and many other names for these types.

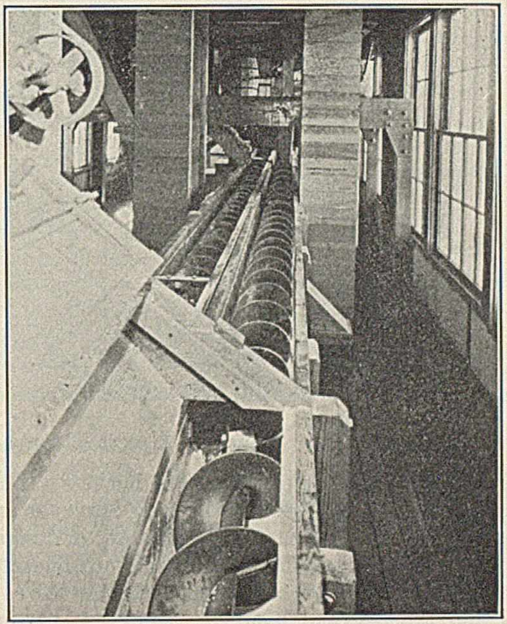
Flight conveyors as a rule are more economical on shorter hauls and lower capacities than belt conveyors. They are obviously more complicated than the belt type of conveyor so there is more to wear out on the flight conveyor. They have the advantage, however, of being more universal in application. There is no limit to the angle of inclination. The same bucket conveyor, for instance, can be used not only for horizontal movement but also for elevating.

The ease of adaption is responsible for the many types in this class of conveyor. The special requirements of the user can readily be met to secure the greatest efficiency of operation. The installation shown in Figure 6 is a special



Courtesy Standard Conveyor Co.

Figure 9—Method of Elevating Sack on Conveyor System



Courtesy International Nickel Co.

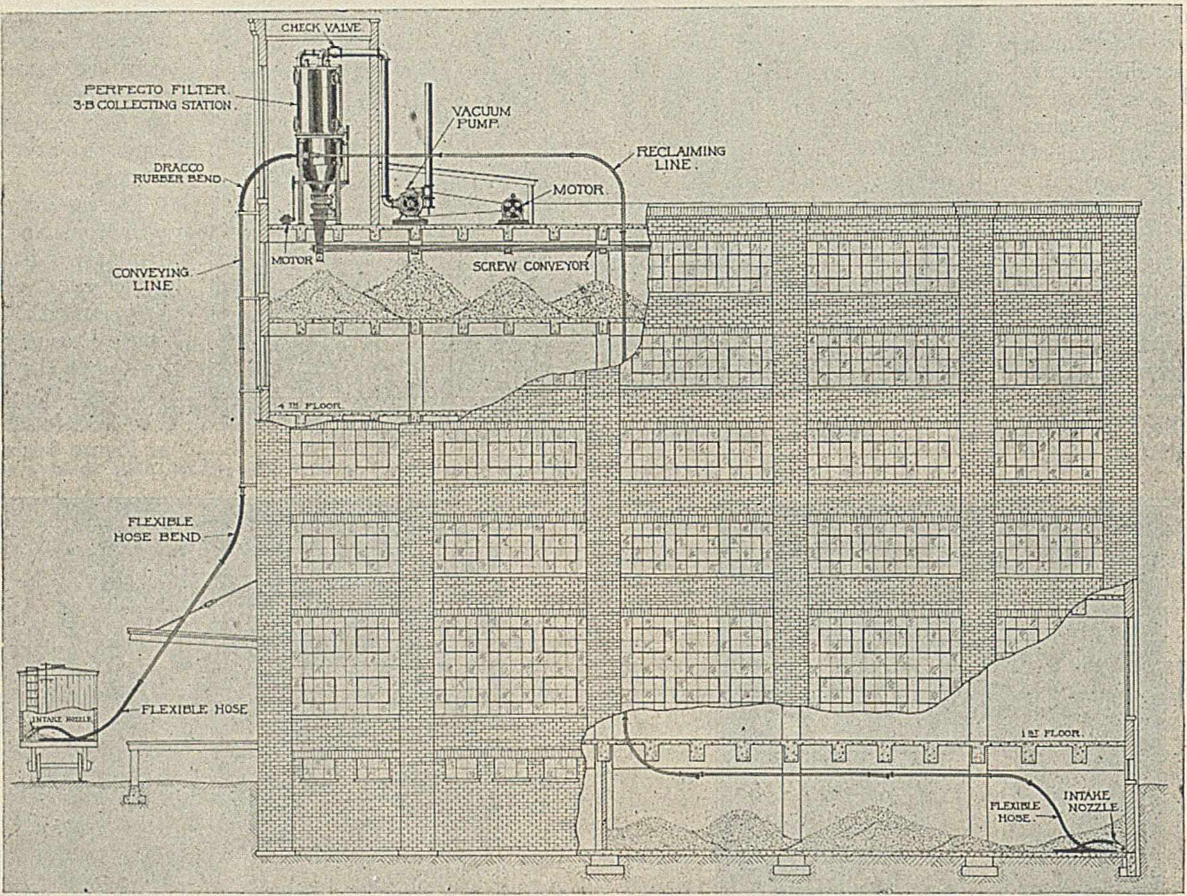
Figure 10—Typical Screw Conveyor Installation for Handling Salt

adaption of the bucket type of elevator for use in a salt plant. To avoid corrosion the buckets are made from monel metal and mounted on a belt instead of a chain. Figure 7 shows a more typical example of the flight type of conveyor, being mounted on a chain.

A very special type of flight conveyor is shown in Figure 8. It can readily be seen that the handling of so large a quantity of sacks in storage is a real problem. The equipment shown can be used both for piling the sacks and for removing them again to be loaded for shipment. The installation is of unit construction so that it can be easily shifted. Because these conveyors are portable, they are sometimes called "portable conveyors." The boom at the end of the unit shown in Figure 8 can be raised or lowered according to the height of the pile. Figure 9 shows a permanent mounting of the same type of conveyor for elevating similar sacks to an upper floor.

Apron conveyors are similar in construction to the slat type of conveyor shown in Figure 7, but present a continuous platform for moving materials. The wood type of apron conveyor is analogous in function to the gravity roller conveyor and is widely used for moving containers such as boxes, cartons, and barrels. Steel apron conveyors are frequently used for handling loose materials.

The bucket conveyor and elevator is very old and widely known. Similar to it in principle is the tray conveyor. The trays are simply flat-bottom, shallow buckets. There is little distinction, if any, between the tray conveyor and the pan conveyor in which the carrying units vary in design from the flat tray to what amounts to a continuous-bucket type, and the selection between these types depends on the capacity required and the material handled. They are particularly useful for carrying heavier loose solids as well as solids that have a high moisture content.



Courtesy Dust Recovering and Conveying Co.

Figure 11—Diagram Showing Handling of Soda Ash with Pneumatic System

An entirely different principle is utilized in the scraper type of conveyor, where the material being handled is simply scraped along through a trough by plates. Loose solids can be handled and dropped out through valves in the bottom of the trough wherever desired. In the chain conveyor the principle is very similar. Instead of being scraped through the trough, the material is carried along by ordinary conveyor chains set in the bottom of the trough.

Screw Conveyors

A fourth class of material-handling equipment is the screw or spiral conveyor, as shown in Figure 10. These conveyors are adapted particularly for handling loose materials on a horizontal plane for short distances. They can be loaded at any point along the screw through a chute and can likewise be discharged at any point through valves in the bottom of the trough. The advantage of this type of conveyor where it is desired to distribute bulk solids in large storage bins can readily be seen.

There is little variation in the types of screw conveyors. There are several designs of flights or screws ranging from the long, continuous-flight type to the small, sectional-flight type, where each section is made from a single disk, and from the open-flight type having only a spiral edge and open core to the solid type as shown in the illustration. For some substances to be handled in the chemical industries special materials of construction are required.

Pneumatic Conveyors

For handling loose material with a low moisture content the pneumatic conveyor is sometimes economical. The pneumatic conveyor consists of a vacuum pump that draws air through a hose to an air-filter station and then discharges it into the atmosphere. Loose material can be picked up and carried through the hose with the air as far as the filter station, where it is filtered out and dropped into a hopper for further distribution.

A typical pneumatic conveyor installation is shown in Figure 11. It shows how materials can be picked up either from a railroad car or from a storage bin, discharged into a screw conveyor, and distributed over a live storage floor, where it is ready for processing. Distance is of comparatively little importance in pneumatic conveying, since the material once in suspension in the air requires little additional power to move it over long distances. Pneumatic systems are frequently used to move materials from one building to another 400 to 500 feet away. The conveying lines can be either overhead or underground.

Installations of this kind have already been made in a number of chemical plants for handling such materials as lithopone, arsenic blue fume, phosphate rock, white clay, acetate of lime, soda ash, granulated alum, sodium bisulfate, lead oxide, etc.

Other Types of Conveyors

There are other types of conveying equipment considerably less common in the chemical field, but which are being adapted to this service as the needs develop. Among these are the drag scraper for storing and reclaiming coal and for handling sand, and the skip hoist which has been a common means for handling coal and ashes in the power plant. These have been applied in the chemical plant for handling large quantities of such materials as salt and sulfur in storage or for loading and unloading railroad cars, and will be discussed at greater length in a subsequent article.

The Trend of Filtration[1]

Arthur Wright

Filtration Engineers, Inc., Newark, N. J.

The unit process of filtration is a part of the manufacture of so many chemicals and allied products that to make a generalization of the present trend of the art would indeed be both bold and erroneous. There are, however, some outstanding tendencies that point to the future and are probably best appreciated by a résumé of the progress made to date.

Progress in Filter Construction

If we were to go back to the end of the last century, we would find that filter manufacturers were developing best mechanical means for accurate machining of plate-and-frame and recessed-plate filter presses. These machines constituted at that time a big advance in the filter art by accommodating a large filter area in a small floor space. The filter area of a suction-box filter was but a small fraction of the area of a filter press requiring the same floor area. This advantage is still a real consideration for many chemical manufacturers. Also, it must be remembered that accessibility to and changeability of the filter cloth in the plate-and-frame press are important advantages as evidenced by its continued use and demand in so many of our progressive plants.

George Moore, the inventor of the Moore leaf filter, was the first to appreciate that a filter could do a greater duty than "separate solids from liquids." His monumental work at the beginning of this century, in the recovery of the gold dissolved in the cyanidation of gold ores from the filter cake, established the washing phase of the duty of filters.

David Kelly, of Kelly filter press fame, and E. J. Sweetland, of first the Sweetland Filter Press Company, then the United Filter Press Corporation, and now the Oliver United Filters Corporation, expanded Moore's work to accomplish the same ends with a greatly reduced filter area by housing the leaf construction within pressure shells.

E. L. Oliver, of Oliver Continuous Filter Company (now Oliver United Filters Corporation), made practical continuous filtration of Moore's idea of unrestricted cake formation and displacement washing. The thousands of Oliver filters in daily operation are proof of Oliver's contribution to the art of filtration.

Filtration Engineers, Incorporated, has helped along the cause of better filtration in the conveyance of cake from the filter to automatic drier and in ingenious cake compression and non-atomizing wash.

If we take a proper appraisal of these advances we can appreciate that each step has been prompted by economic conditions. The reduction in floor space of the plant-and-frame presses made possible many filter stations that would never have been economically practical were the same capacity to be handled on gravity, bag, or bed filters. Moore's filter revived the cyanide industry, and even made profit in refiltering old tailing piles rich in gold lost under the former system. Kelly and Sweetland reduced labor costs in many processes and enabled American manufacturers to meet labor costs of foreign competition. The tremendous capacity per unit filter area on Oliver's filters, in addition to the minimizing of labor, filter cloth renewals, power, and other costs of filtration, made economically possible the establishing and maintaining of many plants. The American Continuous filter, at first simply a competing unit to the Oliver, is still in demand wherever large areas in small floor space are desired for continuous filters.

The FEinc filter was born out of the economic idea of uniting in one machine the two unit process of filtration and drying. Its principle of cake conveyance and cake conditioning makes this filter successful in the pottery, paper, cement, sugar, and chemical industries, as well as in the dewatering of municipal sewage solids.

If economic considerations have been at the base of filter advancement, they are likely to mold the trend of the filters in the future. We can predict that, whereas the duty of filters has progressed from "separating solids from liquids" or "getting a good hard cake" to the combination of one or all of the phases of clarification and simple dewatering—i. e. cake washing and cake dewatering; cake conditioning for drying or calcining—the duty may be expanded to include a possible leaching of solubles, impregnation of the cake, or other processing of the solids. We know, however, that discharging the cake from the filter cloth will ever be the fundamental of every successful filter.

Discharge

Complete discharge of the cake is today the most vital consideration in filter operation. We may have advanced in our

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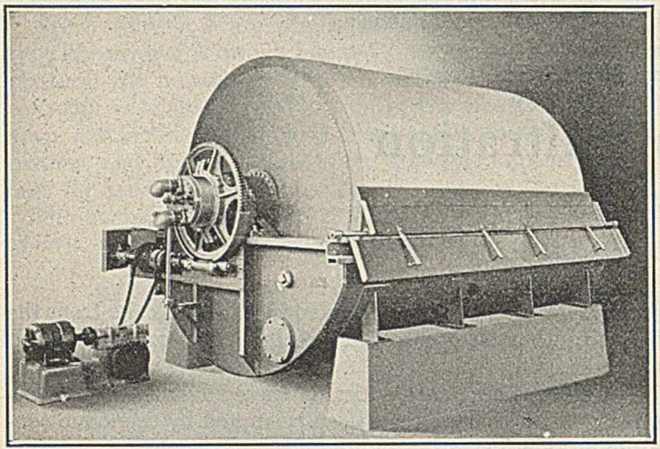
[1] Received March 16, 1929.

efforts to effect automatic filtration, but no progress has been or will be possible unless the specification of "porous filter medium" is obtained and maintained. No manufacturer of filters and no chemical engineer with experience would think of applying automatic filters where the filter cloth is liable to be plugged up or become impervious. There are instances where "bull dog" tenacity has prolonged the use of continuous filters by renewing filter cloth every few days, but from the viewpoint of good operation this is no advance to the art.

Automatic Filtration

Where properly applied, automatic filtration represents the present trend of the art and must be the line of attack for the future. If truly automatic, the operator becomes merely an observer and the operation independent of the observer's personal efficiency. When the control is kept in the hands of the plant executives, constant uniformity of results is a possibility. What greater work can there be for a piece of equipment than to deliver always a uniform product at uniform or controllable rates?



Oliver Continuous Filter

If the machine can deliver this uniform product, in what condition shall that product be? Here lies the controlling factor in present-day filtration. With a definite objective as the goal for the work to be performed by the filter, the designer has a clean-cut job and the operation every chance of success. To have an indefinite objective is the surest means of effecting an unsatisfactory installation.

Clarification

If clarification is the main duty required, then the emphasis in the design is for quality of filtrate and maximum period of filtration. In intermittent filters this will require a technic of operation to obtain a coating upon the filter cloth that will insure the desired clarity. The time cycle of filtration will be prolonged to the economical limit—that point beyond which the flow is too small for maximum production. In automatic filters the design will require that the cloudy filtrate be separately collected and returned for refiltration and the submergence of the drum increased to 70 to 75 per cent or more, where possible.

When handling sugar liquors, corn sirups, malt liquors, and other food products, clarity of filtrate is a prime objective of the filter installation. In metallurgical work the clarity of the dissolved metal solution determines the quality of the reduced metal and is obviously a vital point in the flow sheet. When clarifying waste waters, either to prevent stream pollution or to recover valuable products (as stock in white water in paper manufacture), the clearer the filtrate the better the operation. Chemical manufacturing abounds in examples where clarification is positively necessary. In the textile industry it is also a prime requisite, as in the manufacture of the cellulose products, rayon, celanese, etc.

Washing

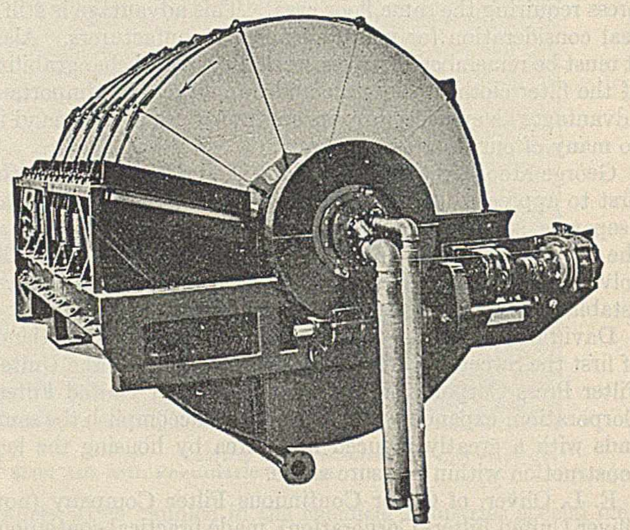
The progress to date in freeing the solids in the filter cake of the soluble in the voids of the cake has been outstanding. We are accustomed to think of this success as an ordinary everyday achievement and yet we continue to make further advances. The trend will ever be toward that goal—wash-water consumption equal to the volume of the voids of the cake. We are experiencing many plants whose wash-water consumption is equal to or slightly less than the volume of the cake. Often this achievement will not lower the density of the combined strong and weak filtrates 1° Bé.

In intermittent filters the technic of withdrawing the excess unfiltered slurry and filling with wash water is simplified by filling with a clouded wash water. In automatic filters the design requires that the wash water be applied before the cake surface loses its uniform resistance and that the wash water application be sufficient. By applying excess water to the surface of the cake every square inch is thoroughly wetted. In such a design provision is made to shed off the excess water to prevent contamination of the unfiltered liquor.

Washing filter cakes is a common practice in practically every industry in which a valuable liquid must not be lost in the wasted cake; where a pigment or other valuable solid is depreciated by the presence of a water-soluble; or where the discharge of an otherwise sticky, tacky, and difficult material is rendered easy after washing the cake. In the zeal to obtain better washing of the cake, it must not be forgotten that the adsorption power, capillary attraction, and those other forces that hold surface liquor are better removed after some upsetting condition as repulping, neutralizing, etc.

Dewatering

Whether we wash the cake and then dewater, or dewater the cake only, we find the automatic filter is designed to provide sufficient time for this work. Filters of as low as even 20 per cent submergence are the rule.



American Continuous Filter

The dewatering of a filter cake is the extraction of the liquid from the voids of the cake. If the voidal space is minimized, the job of dewatering is small. Here lies one of the secrets of the dewatering efficiency of plate-and-frame presses. In automatic filters prevention of crack formation by flappers or by cake compression, and crack closing by compression belts and rolls function to deliver drier cakes.

The value of cake dewatering is quite obvious when the cake is subsequently dried or calcined. In many plants maximum dewatering is just as essential, however, in order to get the best soluble recovery.

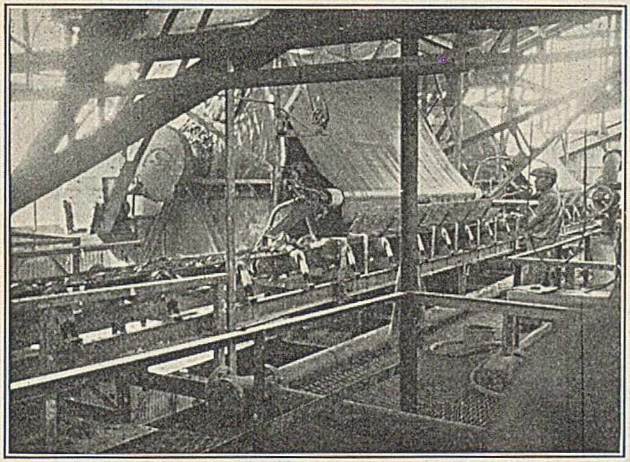
It is interesting to note the value of adequate dewatering for those manufacturers who feed the cake to kilns or calciners. Removal of even 0.5 per cent moisture may be sufficient to prevent that sticky texture of cake which is so prone to ball up, ring up, and spill back, and deliver a friable product free from tackiness.

Function in the Flow Sheet

The dependence of good kiln operation or good drier practice upon good dewatering effect on the filter marks a trend in filter development. Unit processes are seldom independent operations and this is particularly true of filtration. Therefore, in the flow sheet the filter lies between two other processes. To make each unit dovetail so that the operation of the plant is easily controlled, efficient, and economical is a matter of good engineering as well as design of machines.

When there is an optimum condition of the slurry for best filter operation, this must be obtained and retained. Perhaps the case calls for a critical control of the pH; it may be a matter of critical temperature, of concentration of solids, thorough mix of all solids of suspension, etc., etc., in order to get good filter performance. There is little excuse today for failure to maintain such conditions. Automatic chemical feed devices are used to hold a constant pH as determined by a potentiometer, in such a variable as raw sewage. Automatic temperature controls are likewise successes and thickening devices, improved agitators, etc., are almost commonplace.

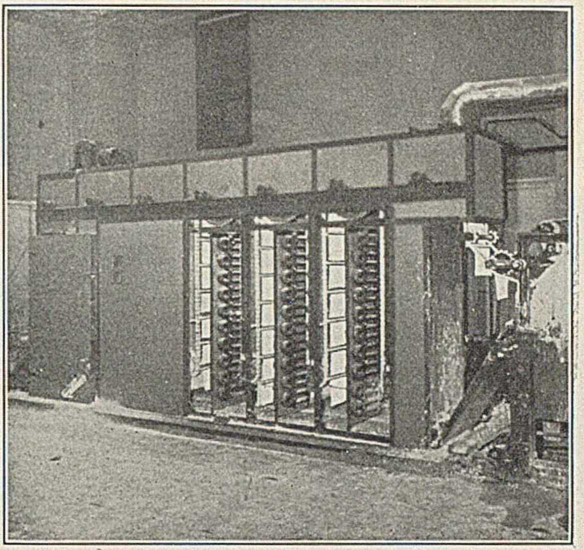
A filter is a mechanical unit and all its functions are mechanical. It is no worker of magic, capable of agglomerating colloids, feeding in a neutralizing agent, or introducing heat units. It must take the slurry fed to it and handle it. Its capability is obviously dependent upon the proper functioning of prior processes.



FEinc Filters Dewatering Raw Cement Slurry Preparatory to Firing in Kiln

When the objective of the filter is to clarify the liquid of the slurry for subsequent evaporation, distillation, precipitation, or whatever process follows, the clarity must be uniform. The trend in this phase of filter work is to put more and more dependence upon the initial solids filtered on the cloth rather than on the cloth itself as the filter medium. Thus, when a filter aid is used, we find greater quantities used per ton of liquor. Economy requires recovery of this aid and recovery plants are now the vogue.

When recovering the soluble from the cake, it is not enough to minimize the loss in cake by washing, but this must be accomplished without undue consumption of water. There are many instances where displacement wash is used for a rough recovery, the cake being repuddled and refiltered. This is to many plants a recent departure made attractive by the use of automatic filters, with which the repulping and refiltering are continuous and automatic. The ideal wash is, of course, true displacement of the soluble in the voids of the cake by the percolating wash water. The approach to this goal is a matter of water application. The cake must be maintained in its equi-resistant condition and the water uniformly distributed. To overwet the surface of the cake without eroding the cake with the excess is the trick which has proved of real benefit.



Continuous Recirculation Drier, Taking Cakes Direct from Filter

When final drying of the cake calls for maximum dewatering, recent practice dictates that we maintain an equilibrium with the other objective—capacity of the filter. A product may be dewatered 0.5 per cent more by lengthening the time of dewatering 50 per cent, but when this requires more machines, more power, and increased filter cloth and renewal expenses, it is a loss and not a gain. The product leaving the filter should be in prime condition for drying, and as dry as is economical. The economical limit in mechanical dewatering is reached when the operating and capital charges for the filter operation exceed the operation and capital charges of the drier lifting the water by B. t. u. transfer.

Conclusion

The present trend is to introduce automatic filters for their ability not only to save labor, filter cloth costs, and other such tangible savings, but to insure continuity and uniformity of product independent of the personal efficiency of the operator. With this we find that filtration is an intermediary unit process, the functioning of the filter depending upon the condition of the product being fed to it, and its end products should be in a condition best for the subsequent process. The objective of the filter must be definite so that the design may be adequate, the construction correct, and the operation economical and efficient.

The future is bright for better filtration.

The Progress of Industrial Heating by Oil Circulation[1]

Alexander B. McKechnie

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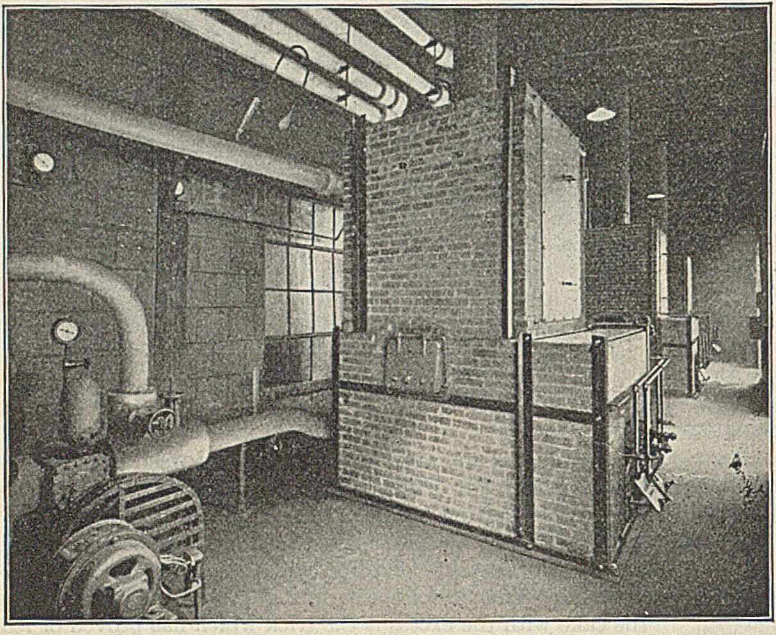
INDUSTRIAL heating by oil circulation has been successfully applied to high-temperature heating processes in many industries for about fifteen years. Naturally the equipment has gone through many important changes toward improvement, but the basic principle of operation is unchanged. The size of installations has increased as well as the number of processes to which it has been applied.



Three Systems Installed in a Chemical Plant in 1919

Description of System

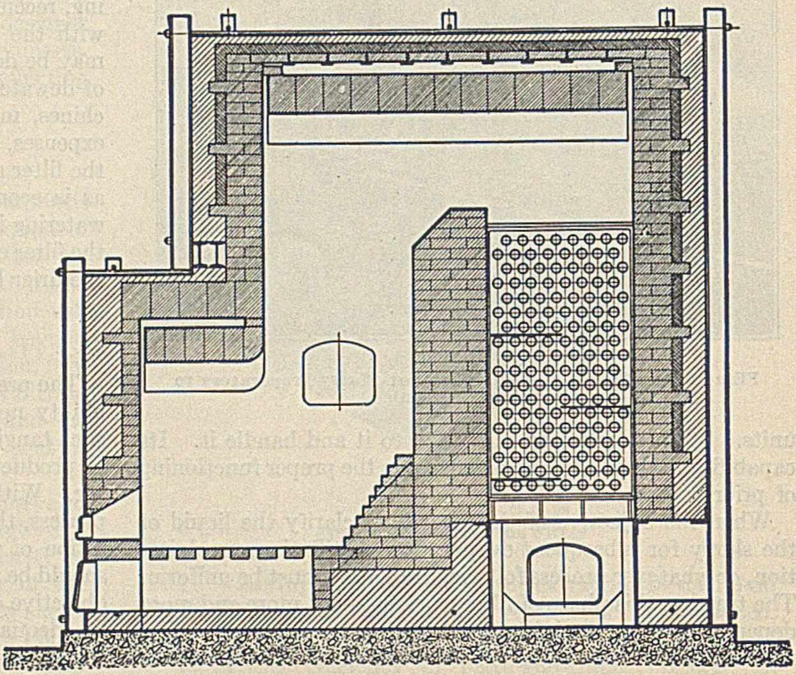
A heating system in which a high-flash oil is used as the transmitter of heat is analogous to a hot-water heating system, but instead of depending upon thermal circulation to carry the heated oil to the point of heat consumption, a circulating pump is employed to give a high velocity of flow. These systems operate at practically negligible pressures of about 10 to 15 pounds on the hot-oil supply and return mains. Because of the low pressures it was at first considered a very easy task to build a heating plant and distributing system of this kind. Actual experience, however, proved the fallacy of this thought, and it was soon learned that circulating oil under high temperatures up to 600° F. (316° C.) could only be handled in equipment of the most rugged construction, properly designed to avoid leakage and provide for expansion stresses.

In addition to the problems brought about by the fugitive properties of high-temperature oil, there was also another requiring greater consideration—namely, the delicate nature of the circulating fluid and its tendency to carbonize when overheated in an improperly designed system.

The absorber, or oil heater, should properly be considered the most important piece of equipment in the entire assembly making up a complete system, although there are other parts of major importance from both an engineering and operating standpoint which will be touched upon later. A correctly designed absorber must heat the circulating oil uniformly throughout its entire mass, and without overheating any portion of it. To do this, the oil must be kept moving at a high velocity over the heating surface and the film of oil in contact therewith must be frequently changed by a proper arrangement of oil passages. This requirement takes into account the length and diameter of the heater tubes and the means for connecting them together, also the relation of the heating surface to the heating furnace. The design must also provide for high efficiency in the generation of the heat, as well as its absorption, and all parts must be readily accessible for inspection or repair.

The circulating oil pump should produce a positive and non-pulsating discharge, so as to maintain a uniform and high velocity through the absorber tubes. Only pumps of the most substantial construction, designed for operation under the high temperatures required, can be successful in this work.

There are many commercial oils that have a high flash point, but other properties have to be considered in the selection of the right oil for this work. Some of these are the viscosity of the



Sectional View of Absorber Setting with Downward Draft

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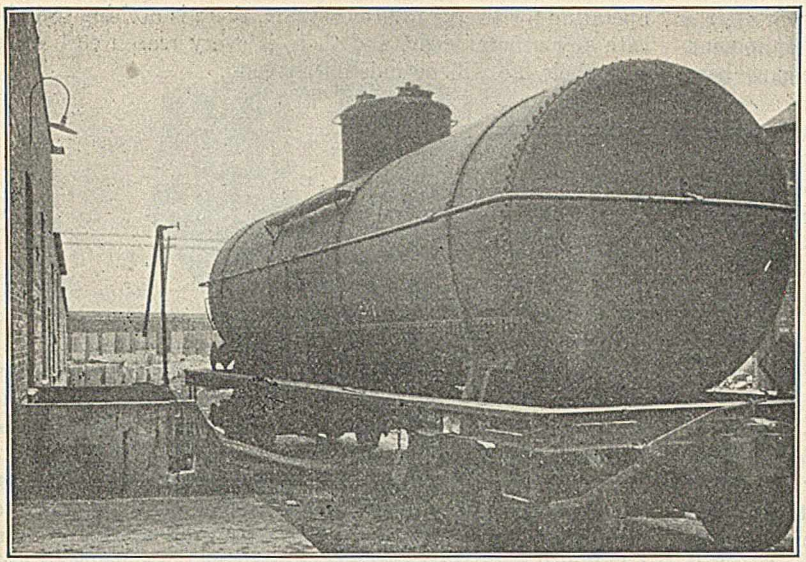
[1] Received February 25, 1929.



Oil-Heated Tank Car; Weight of Contents 80,000 Pounds; Raised to 430° F.

oil, particularly its cold test, also its percentage of distillation at a fixed temperature, and the amount of free carbon produced when the oil is distilled to dryness. The oil recommended for this work is known as "Meprolene," and has been used successfully since these systems were first put into service. Meprolene has the following physical properties:

Specific gravity at 60° F.	0.905
Flash point	597° F.
Fire point	653° F.
Specific heat at 60° F.	0.46
Specific heat at 600° F.	0.71

With the exception of a rare instance or two, it has not been found necessary to withdraw the circulating oil from a system and recharge with a fresh supply.

For convenient and satisfactory operation there are a number of special and patented features, such as the arrangement of the piping in the absorber room between the pump and the heater, with a by-pass loop around the pump to relieve the system from excessive pressure during the starting period, also relief valve location, air separators, safety automatic shut-off valves, etc.

Application in Chemical Plants

These systems have found wide use and large application in many chemical plant processes, particularly for high-temperature heating, evaporating, distilling, and subliming.

In connection with asphalt, it has been used in the high-temperature work such as from 350° to 550° F. required for impregnating transformer coils, cable insulation, saturation of felts for asphalt shingles, paved culvert, coated and duplex papers, molded products, shipping cartons, battery boxes, etc.

The starch industry has made several installations for starch roasting in the manufacture of gums and dextrins.

Wax melting and heating in molded products and the high-temperature heating in rosin purification have taken several systems.

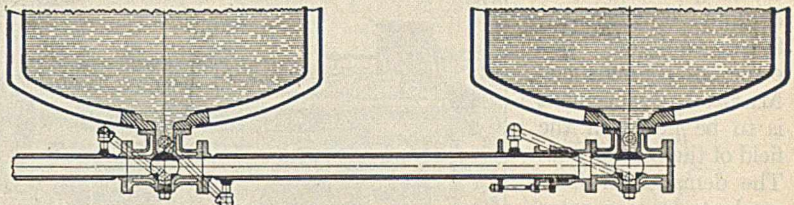
Two installations were made for distillation in the manufacture of toxic gases.

In the vegetable oil industry, where it is necessary even under high vacuum in the deodorizer to obtain temperatures in the vegetable oil ranging from 450° to 550° F., the system has not only proved satisfactory as a means for obtaining temperature, but has also improved the quality of the finished product.

A number of installations are in operation for tank-car heating, with materials that are only sufficiently fluid to pump at temperatures far beyond the range of steam. These particular installations require from 375° to 450° F. in the tank car, and the entire tank is raised to the full temperature before any of the material is pumped from it. The tank cars are especially designed with coils for circulating oil and are properly insulated so that the entire heating process is a very efficient one. These installations are for one or more tank cars per day, and the piping is so arranged that any number of tanks can be connected to the same system if necessary.

It will be noted that many of these materials, such as asphalt, rosin, wax, etc., are substances which are ordinarily solid and require a high temperature to produce a state of fluidity that will render them easily transportable through pipe lines. As an accessory to the high-temperature oil heating system, there is a full line of jacketed piping, cocks, and fittings, made in sizes ranging from $1^{1}/_{4}$ to 4 inches, and larger sizes would be made on demand. In high-temperature installations the jacketed piping is heated with circulating oil; for medium temperatures steam is ordinarily used; and in other cases, such as chocolate and sirups in the confectionery trade, where only a mild temperature is required, hot water has proved to be entirely satisfactory.

To meet the demands of the industries, these systems are built in many sizes ranging in capacity from 100,000 to 2,800,000 B. t. u. per hour, and several absorbers may be connected in battery where necessary. Each different capacity is standardized with its own circulating oil pump and piping, expansion tank, and all specialties of the proper size.



Jacketed Piping 3 × 4 Inches with Cocks Connected to Two Jacketed Tanks. Tanks and Piping Are Heated with Hot Circulating Oil

A fair idea of the size and long life of some of these installations can be gained from the following table:

No.	*B. t. u. per hour*		*Years*
1	1,200,000	Chemicals	13
3	1,600,000	Asphalt shingles and roofing	13
1	1,200,000	Molded wax products	12
2	1,200,000	Starch roasting	8
2	1,200,000	Transformer coil impregnation	5
1	1,200,000	Vegetable oil deodorizing	8
1	1,200,000	Coated papers	8
5	800,000	Chemicals	9
1	200,000	Asphalt molded products	11
3	2,800,000	Vegetable oil deodorizing	5
3	300,000	Chemicals	10

This list only touches upon a few installations, but is representative of them all.

The only moving parts of an installation are the circulating oil and the pump, and the oil naturally protects all metal with which it comes in contact. There is therefore no corrosion taking place, and as the systems are vented to the atmosphere and operate under extremely low pressures, there will be no reason for condemning them after a given number of years, as is the case with pressure equipment. From the condition of the systems which have now been operating for twelve to fifteen years, there is nothing to indicate any general wear, and there is every reason to believe that their life will be indefinitely long.

Crushing and Pulverization[1]

Lincoln T. Work

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As a basic operation useful to the engineering industries in the preparation of materials, crushing presents an interesting diversity and similarity of problems. Mineral ores are disintegrated to prepare them for roasting, leaching, or flotation; coal is crushed to render it suitable for firing; rock minerals are pulverized to make them useful as fillers in rubber and in paints, and as ingredients of glass and pottery; and many other materials are reduced to powder to prepare them for further treatment. Yet, with but few exceptions, the chief aim is to produce surface. Equipment is equally diversified in the many types and construction features of mills. Nevertheless, the problem always before engineers is to select the machine that will deliver the desired product at lowest power, maintenance, and labor cost.

By its very complexity crushing has not been amenable to fundamental scientific analysis. Such a study was limited in the past by the lack of exact methods of measurement; for, at least until recently, it has not been possible to measure fineness accurately below sieve sizes or to evaluate the resistance of any material to grinding. Nevertheless, progress in the development of machinery has been made by empirical methods, keen observation, and the available methods of measurement. Closed-circuit crushing with the aid of liquid or air classifying equipment has come into common use. Marked advancement is to be noted in the field of the colloid mill. The demand for finer products or for more uniform ones is being met. Yet the evidence now available indicates a great loss of energy in crushing and pulverizing. The trend of the future will undoubtedly be toward a more scientific study of the fundamental principles of crushing and of classification, to lower power costs and to produce the desired type of fineness; toward the wise selection of materials and the design for simplicity to insure minimum maintenance; and toward the scientific selection of suitable size units and the use of automatic controls to minimize operating labor.

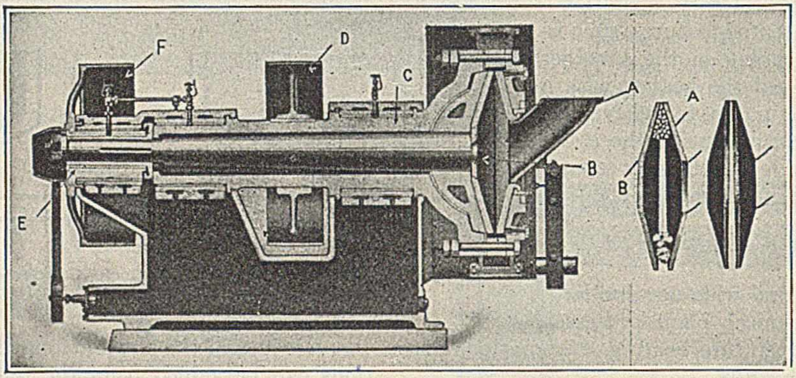

Figure 1—Conical Disk Mill

A and *B*, crushing disks
C, shaft and casing
D, pulley
E, eccentric bearing

Reprinted from "Principles of Chemical Engineering," by Walker, Lewis, and McAdams, published by McGraw-Hill Book Company.

Principles of Crushing

Recent studies in the fundamental principles of crushing have followed three lines: measurement or calculation of surface and its comparison with energy, the fineness characteristics of the product as determined by its inherent nature and by the processes of crushing, and the behavior of materials under the forces of crushing.

The old yet unsolved question involved in the Kick *vs.* Rittinger dispute has been again revived and subjected to new test. Martin[2] has compared the energy consumption in a ball mill with the new surface developed. Silica sand was crushed with 1-inch steel balls in an 18 × 18 inch mill, and surface was measured by the rate of solution in hydrofluoric acid. The energy input was recorded as the difference between that required for driving the mill with and without a charge of sand. As a result of comparing those values with the corresponding new surface developed, he concluded that "in ordinary tube mill grinding the surface produced is accurately proportional to the work done." Recognizing that possible errors might be introduced in the measurement of work done in ordinary mills, Gross and Zimmerley[3] have crushed sand by utilizing the energy of a freely falling body. They have measured surface with their modification of the hydrofluoric acid solution method, and they have found that the new surface produced varied with the energy input. It is their conclusion that "when crushing quartz, the new surface produced is in direct proportion to the work input in accordance with the Rittinger law of crushing." However, it should be borne in mind that these crushing methods measure the over-all energy accompanying disintegration, and that the dissolution test has not yet been rigidly proved to measure surface.

Furthermore, energy input has been compared with surface energy and found to be greatly in excess of the calculated energy needed to develop the new surface.

Observer	Mill	Surface Energy Calcd. by:	Surface Energy Value	Crushing Efficiency
			Ergs/sq. cm.	*Per cent*
Gaudin	Rolls	Edser	920	1.3
Martin	Ball	Martin	310	0.06
Gross and Zimmerley	Stamp	Edser	920	3.0
Gross and Zimmerley	Stamp	Martin	310	1.0

The values of surface energy are somewhat in doubt; but their order of magnitude indicates that a large proportion of the energy input is dissipated as heat or sound.

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[1] Received March 5, 1929.

[2] Martin, *Trans. Inst. Chem. Eng.* (*Brit.*), 4, 42 (1926).

[3] Gross and Zimmerley, Am. Inst. Mining Met. Eng., *Tech. Publ.* 127 (1928).

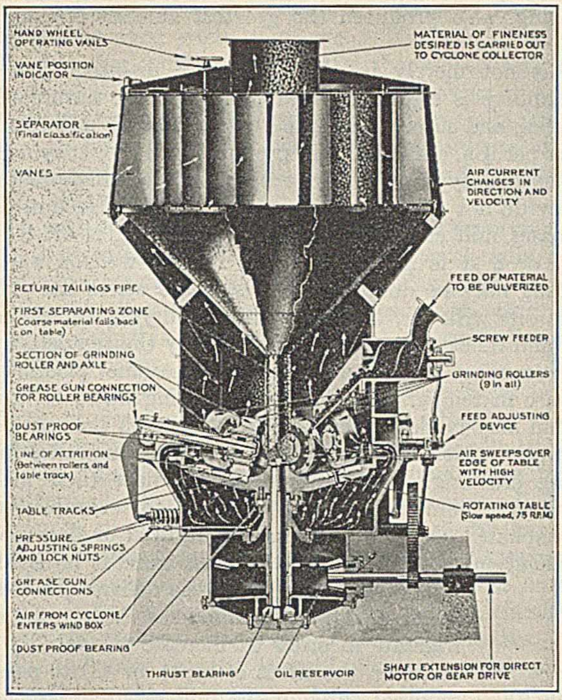

Figure 2—Roller Plate Mill (Bethlehem Pulverizer). Bethlehem Steel Company

These studies have shown: (1) that over-all energy input in crushing quartz is proportional to dissolution rate and probably new surface developed; and (2) that the actual energy needed to develop new surface is but a small proportion of that which is applied in crushing.

Other investigators have studied the fineness of the ultimate material. That is of interest in its bearing on the nature of crushing. Such terms as compression, beam action, shear, impact, abrasion, attrition, and numerous others have been used to picture the typical action of any mill, frequently in cases where no marked characteristic of fineness can be seen in the product. Mathematical analysis of these relations has been attempted, but the variables are so numerous that only probability or statistical formulas have been applied. Martin, Blythe, and Tongue[4] have proposed an exponential relation for quartz ground in the ball mill:

$$N = a\,e^{-bx}$$

where N equals the number of particles in a unit interval of average diameter x, and a and b are constants for each condition of grinding. Gaudin[5] has represented data on the jaw crusher, rolls, rod mill, and ball mill, for quartz, galena, and granite in terms of graded sieve apertures and the percentages included in the sieve intervals. With a double logarithmic plot he found a consistent paraboloid loop in the coarse sizes and a straight-line relation in the fines. He has expressed the latter relation mathematically for calculations into the finest ranges:

$$y = Cx^k$$
$$\text{or } dz = \frac{C}{p-1}\,x^{k-1}dx$$

where y is the percentage by weight in the sieve interval x to px millimeters, and dz represents the amount in a uniform interval from x to $(x + dx)$. C and K are constants. When the rock is not homogeneous, breakage takes place preponderantly at crystal size.

These two relations represent different portions of the fineness curve of a crushed, homogeneous material. The writer[6] has developed for ground sand a dual relation to cover the entire range of fineness. In coarse sizes, usually the upper three-quarters of the range, the relation proposed by Martin and co-workers holds true as a primary function:

$$N = a(10)^{-bx}$$

The plot of logarithm frequency against diameter deviates from a straight line in the finer sizes, and there is added to the primary a secondary relation the cumulative effect of which is expressed for this region as:

$$N = a(10)^{-bx}\,(10)^{q/p}\,x^{-1/p}$$

where a and b are constants from the primary function, and q and p are new constants from the secondary function. The relation has been developed for homogeneous rock and is limited by the presence of unused feed, extreme sizing action in the mill, and classifying action during crushing. These would require supplementary analysis.

Equations of this kind may be used for calculations of surface, average diameter, and other constants; and they indicate the likelihood of less complex functional relations than are implied in the many types of milling action.

With the increase in exactness of measurement and in demands for fineness, the resistance of materials to pulverization has become significant. Take coal as an example. The differences are so pronounced that a mill which will

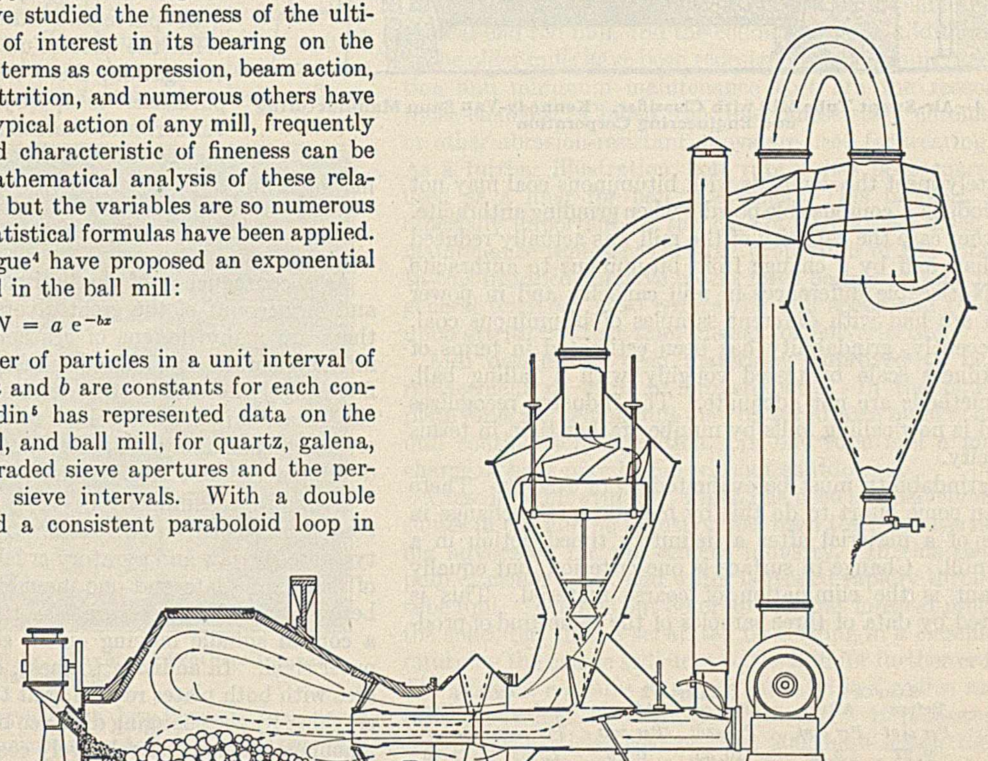

Figure 3—Conical Ball Mill with Air Classifier. Hardinge Company

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[4] Martin, Blythe, and Tongue, *Trans. Ceram. Soc.*, **23**, 61 (1924).

[5] Gaudin, *Trans. Am. Inst. Mining Met. Eng.*, **73**, 253 (1926).

[6] Work, dissertation for doctorate, Columbia University, 1928.

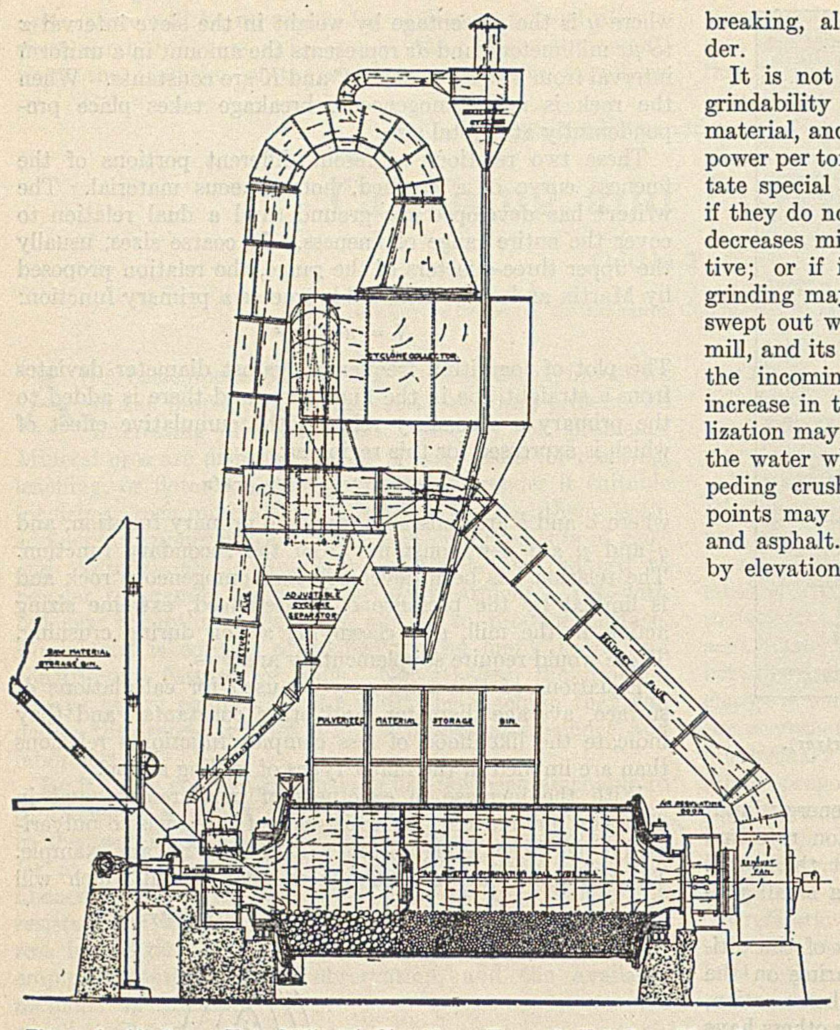


Figure 4—Air-Swept Tube Mill with Classifier. Kennedy-Van Saun Manufacturing and Engineering Corporation

adequately meet the demands with bituminous coal may not even produce a combustible powder when grinding anthracite. In another case the capacity of the mill was actually reduced more than half by a change from bituminous to anthracite coal. Noticeable differences in mill capacity and in power per ton are had with different samples of bituminous coal. Until recently, grindability has been estimated in terms of the hardness scale or tested roughly with a falling ball. These methods are not adequate. The industry recognizes this and is now calling mills by number rather than in terms of capacity.

But grindability must be evaluated more exactly. There has been some effort to do this by measuring the change in fineness of a material after a definitely timed action in a pebble mill. Change in surface is one criterion, but equally significant is the elimination of coarse material. This is illustrated by data of three samples of the same kind of product.

Mesh	Sample 1		Sample 2		Sample 3	
	Before	After	Before	After	Before	After
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
On 16	9.27	3.43	10.55	0.66	12.53	3.46
16–20	89.23	68.18	87.81	21.15	67.12	28.18
20–24	1.23	10.84	1.24	42.24	18.36	31.15
24–35	0.15	6.18	0.17	16.95	1.19	15.50
35–50	0.06	2.46	0.17	5.29	0.48	6.25
Minus 50	0.06	8.91	0.06	13.71	0.32	15.46

The initial materials are essentially of the same size. Sample 2 shows much more pronounced elimination of coarse material than Samples 1 and 3; yet Sample 3, which resisted breaking, also produced the greatest amount of fine powder.

It is not merely in the manner of disintegration that grindability is significant. Moisture, plastic nature of the material, and susceptibility to heat may affect mill capacity, power per ton, and quality of product; and they may necessitate special types of mills or special processing procedures if they do not altogether prevent milling. Surface moisture decreases mill capacity. Preliminary drying is often effective; or if it is not undesirable, further wetting and wet grinding may be done. In mill systems where fine dust is swept out with air, there is a definite drying action in the mill, and its extent may be controlled by the temperature of the incoming air. Some materials become plastic with increase in temperature. Salts containing water of crystallization may be decomposed on heating, with the result that the water which is evolved acts as surface moisture in impeding crushing. Materials which are near their melting points may be softened with heat—as, for example, sulfur and asphalt. Organic dyes may be injured or decomposed by elevation of temperature. In such cases it is usual (1) to choose a type of mill to deliver the desired fineness with a minimum of heat; (2) to refrigerate in order to increase grindability and to lessen the effect of heat; or (3) to pass the material through the mill rapidly, remove the portion which is sufficiently fine by sieves or air separation, and return the oversize to the mill for further reduction.

There is undoubtedly need for a thorough study of grindability and the correlation of this with actual crushing data. It is particularly necessary in those fields where milling costs are a large proportion of the total, as with pulverized fuel and Portland cement. With the successful conclusion of such an investigation, there will be less difficulty for the purchaser to specify the proper size of pulverizer, and there should result greater meaning to the contract guarantees of the mill manufacturers.

Types of Mills

As a consequence of the limited knowledge of mill action and on account of the great diversity in crushing problems, there are many designs of crushers and pulverizers for use in the chemical and related industries. These can be classified roughly according to the nature of their action. Such a classification is presented here to portray the entire range of crushing machinery. Special note will be made of new developments and future trends.

DIRECT PRESSURE MILLS—The material to be crushed is compressed between two faces. The usual examples of that type are the jaw and gyratory crushers. The former consists of one fixed plate and one movable plate at an angle to it, between which the pressure is exerted. The latter consists of a conical spindle moving on an eccentric within a tapered outer shell. In addition to these, one of the disk mills operates with both plates revolving at the same speed, and effects crushing by the changing distance between the plates. These machines are used for relatively coarse crushing and deliver a product having appreciable amounts over 4 mesh. The angular relation of the plates in these crushers makes possible a large reduction in diameter, for breakage first takes place in the wider section and further reduction takes place in the narrower section.

ROLLER MILLS—Crushing takes place between a roller and a fixed or moving surface. The action may be directly applied to the piece or, as with the crowding at finer sizes, it may be between particles as well. The single roll is a coarse crusher which breaks the material against a rigid face. Rolls are usually used for intermediate grinding, and they crush the material between the surfaces of two rotating cylinders. In differential rolls, which consist of pairs of rolls revolving in opposite directions, material is finely pulverized between the faces. For fine sizes of certain materials the Chilean mill, which consists of a heavy wheel revolving in a pan, is used with a wet or dry charge. Several mills of the roller type are used for pulverization. They depend upon the action of rollers operating on spindles in a die-ring, large balls being pushed in a die-ring, or rollers or large balls acting on a rotating plate.

Tube Mills—Machines of this general class act by the tumbling of crushing members together with the charge in a slowly revolving drum. The ball mill is a cylinder filled with balls 2 to 4 inches and more in diameter. A longer mill with smaller balls or slugs is used for finer grinding and is known as the tube mill. When balls of many sizes are rotated in a conical-shaped drum, the large balls segregate themselves at the larger diameter and the smaller ones at the end. It is claimed that such a mill exerts a classifying action on the material, passing only the finished sizes. The rod mill, and more recently the self-aligning conical-end rod mill, employs a charge of rods. As its action is more analogous to the roller mill, the rod mill eliminates coarse particles rather than producing fines.

These machines may be used as batch or as continuous mills. In the former event the desired product is secured by operating for a specified time; in the latter case rate of feeding solid determines the fineness. The charge may be ground dry or wet with a fluid such as water or oil. They are all pulverizing mills.

Beater Mills—Machines of this type consist of a rapidly revolving beater in a casing. The hammer mill is so named for the bars or paddles attached to the rotor, which beat the material about within the casing to cause breakage. These mills are designed for intermediate breaking or for coarse pulverization of easily fractured materials. Another machine of this type is the cage mill, which consists of concentric cages revolving in opposite directions at high speeds. The material is beaten to finer size as it passes by the cage bars. This mill is used on materials where disintegration of clusters or agglomerates is required rather than actual pulverization.

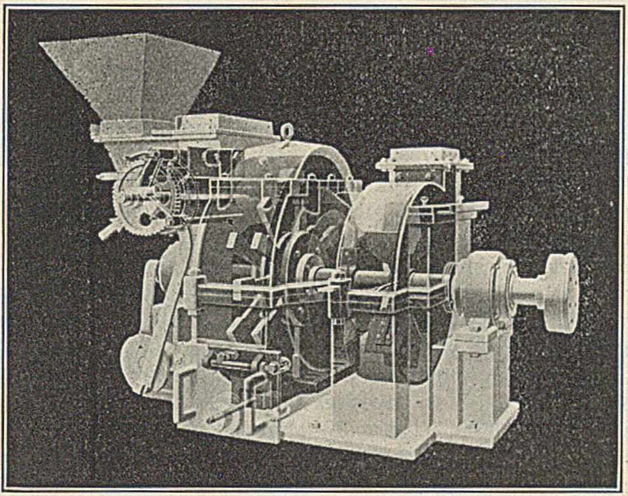


Figure 5—Hammer Pulverizer. Raymond Brothers Impact Pulverizer Company

Revolving Plate Mills—In such machines material is disintegrated between the faces of two plates revolving in opposite directions, or with a differential of speed. Disk mills are used in the intermediate to fine range. For finer materials stone mills are used. The solid or paste is fed through the center of one stone. By the action of the grooves and by centrifugal force, the material feeds outward between the plates and is discharged from the surface. Mills for disintegration of pulps to colloidal sizes are usually of the revolving plate type. They are operated at high speed with positive feed and with close clearances, the viscous flow of the fluid being the force for disintegration.

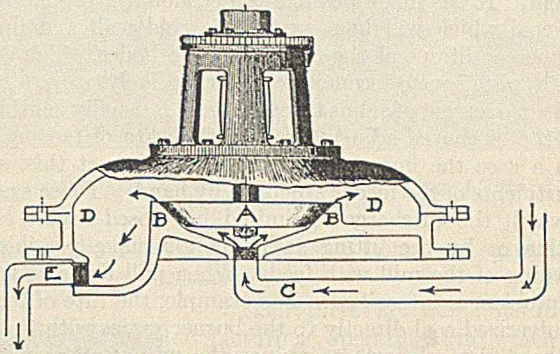


Figure 6—Colloid Mill. Premier Mill Corporation

A, conical rotor
B, fixed crushing face
C, feed pipe
D, casing
E, outlet pipe

Developments in Crushing Machinery

The more significant recent developments in crushing and pulverizing are: new designs of mills, more wear-resistant materials, simplification for repairs, new applications of closed-circuit grinding, air-sweeping of mills, and automatic control.

The newer mills are those of the revolving-plate type, the conical-end rod mill, and the colloid mill. In addition, many of the older mills have been redesigned. Continuity of operation and minimum maintenance cost are the reasons for those changes. Chilled iron, manganese steel, chrome steel, or other abrasion-resistant alloys are used for wearing parts. As a further illustration, soft rubber has been successfully used as a liner for ball-tube mills. This problem is also especially important in the case of high-speed mills, where maintenance represents a large proportion of the total cost. In this instance abrasive blocks have been proposed, but the general tendency is to reduce the mill speed and to depend upon attrition rather than impact for pulverization.

Mill design has been materially improved to facilitate replacement of worn or broken parts. In the new roller plate mills a crushing unit may be withdrawn quickly and the mill continued in operation. In one tube mill a make-up charge of balls may be fed without shutdown.

Closed-circuit grinding, which has been extensively used on slimes in the mining industry, has been tested and is now being advocated for the cement industry. In this scheme a pulp of cement rock and water is passed rapidly through the tube mill. There is but 30 or 40 per cent finished product in the solid, but that is separated by settling in a classifier and returning the coarse sediment to the mill for further crushing. The product contains less fines but also less coarse material than is obtained by single-pass grinding. It produces good clinker, as particles coarser than 200 mesh lessen the completeness of the reaction. Mill capacity is increased 50 per cent, while wear on liners and grinding media is reduced 25 per cent.

The same principle has been applied where the product must be dry. Roller, beater, and tube mills are often swept with air to remove the fines and leave the coarse material for further grinding. In addition to the savings in power and maintenance, the air may be used to dry the feed. The coal used in firing the marine boilers was at times dripping wet at the feeder; and although the capacity was lowered, the mill showed a satisfactory performance. Inert gases are used in place of air to reduce combustibility, as for sulfur and occasionally for powdered coal. Most of the mills employing air classification do not effectively eliminate the coarser particles. Air separation and classification is a field of great promise. It has effected economies in fuel pulverization and should do likewise in the final grinding of cement. It has made possible the economical production of fine coal which will burn under the cold wall and limited volume conditions of the Scotch marine boiler. The analogous application to locomotive boilers is likely.

The movement of solids through a mill is usually continuous and the discharge adjusts itself to this rate of feeding. In such a case the fineness varies; and to correct this, slight adjustments of the feeder are made by hand. Those systems in which the discharge is limited by closed-circuit classification or by the lifting action of air make possible the crowding of the mill with feed. When mill demand varies, the problem is intensified. For example, the rate of feeding of pulverized coal directly to the burner varies with the load on the boiler. Efforts to reduce the mill-attendance labor now necessary and to secure optimum grinding efficiency by automatic controls have not been entirely successful. The increased current that is required of the mill motor to meet production demands with a crowded machine is a possible answer with certain types of pulverizers.

The state of the art and the present trends have been outlined, with illustrations from the more important fields. The applications of milling to many kinds of products are too numerous to mention and can be found in trade catalogs. Costs are so largely influenced by the material, its initial and final fineness, its grindability, its moisture content, that the limited figures which could be given here might easily be misleading.

Conclusions

1—Recent studies have shown that the over-all energy of crushing quartz is proportional to the dissolution rate and probably the new surface developed and that the energy theoretically necessary to develop new surface is but a small proportion of that actually used.

2—With the more exact methods of measurement of fineness, mathematical analysis of fineness curves has become possible. The statistical relations so far developed are available for calculations of surface and other functions. They suggest less complex relations than have been applied to milling.

3—The fundamental resistance to pulverization of any material and the resistance under operating conditions are important and unmeasured properties, which must be quantitatively evaluated.

4—A rough classification has placed the mills of interest in the chemical and related industries as (1) direct-pressure mills, (2) roller mills, (3) tube mills, (4) beater mills, and (5) revolving plate mills.

5—New developments in crushing and pulverizing are: novel designs of mills, more wear-resistant materials, simplification for repairs, new applications for closed circuit grinding, air-sweeping of mills, and automatic controls.

Manufactured Weather[1]

An Aid to Modern Industry, Health, and Efficiency

D. C. Lindsay

Carrier Engineering Corporation, Newark, N. J.

LOOKING backward is of value primarily to aid us in laying out future plans. Of course, it is a pleasant pastime to reminisce, but this is hardly the time and place. So in trying to present to the reader an understanding of the place which the comparatively new science of air conditioning holds in the field of human endeavor today, we may pass very quickly over the few years and events which have made it possible for us now to create and maintain within doors almost any desired atmospheric conditions with reference to temperature, humidity, air purity, and air movement.

The crude forms of ventilation existing slightly over a quarter of a century ago could not be classified as the science of air conditioning. We had some fans for air movement; automatic temperature control for heaters was in its early stages of development; in some industries manually controlled methods of humidification through the ejection of steam or water into the air within the room had been practiced. The physical laws governing the quantity of moisture existing under various conditions in our atmosphere had been subjected to very little investigation except as a factor in outdoor weather. The effect of atmospheric moisture and temperature variations upon many materials had been observed and had been responsible for the few devices and attempts which had up to that time been applied to counteract these influences.

In 1902 Willis H. Carrier, an engineer just out of college, was given the problem, in the course of his employment by a well-known manufacturer of fans and heating equipment, of devising a means to reduce and control the humidity in the plant of a lithographer. The purpose was to eliminate the many difficulties arising in the application of several successive colors to paper which varied in size according to humidity variations between impressions. The solution of this problem opened the road to investigations and the development of equipment which have today assumed vast importance and which form the basis of the science which we now term "air conditioning."

The now common spray-type, central-station humidifier was then evolved. The dew-point control, by which the moisture content of the air leaving the spray chamber is fixed through the thermostatic control of the temperature of the spray water, was a part of this development.

The same experiments soon brought about the discovery that the most efficient method for cooling and dehumidifying —i. e., reducing the moisture content of air—is to subject it to a finely atomized spray of water cooled to a predetermined temperature; this, in contrast to some earlier cumbersome sets of pipe coils through which refrigerant was passed and over

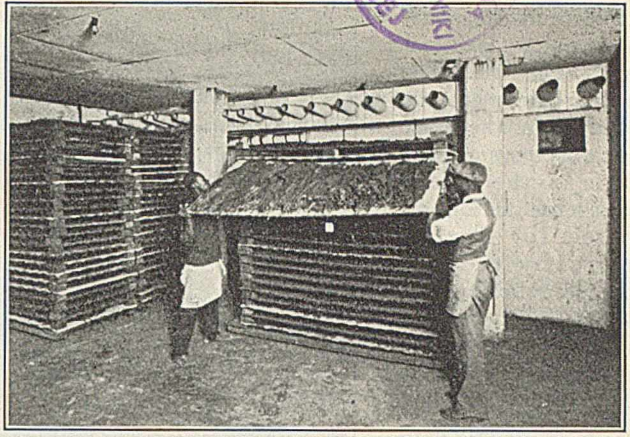
[1] Received March 18, 1929.

which the air was blown, depositing frost and dirt on the surface of the pipe.

These investigations likewise led to an understanding and the mathematical rationalization of the laws governing the heat and moisture content of our atmosphere. This rationalization was presented several years later by Mr. Carrier before the American Society of Mechanical Engineers.[2]

Industries were waiting for these developments. As early as 1905 textile mills seized upon central-station air conditioning and humidification to create and maintain atmospheric conditions suitable to the handling of the delicate hygroscopic fibers of cotton and silk. Textile mills had always been fighting this problem. It had made necessary the location of mills only in favorably humid climates. But new problems had arisen. High-speed machinery had arrived and with it the liberation of great quantities of mechanical heat to counteract the normal climatic humidity within the mills. There is today no modern textile mill without some means of air conditioning or controlled humidification, and this development has made possible the erection of great mills in the midst of the cotton fields in the South, without regard to what previously would have been forbidding climatic conditions.

Other industries followed in the adoption of air conditioning as a factor in efficient and controlled production. Today we can number by rather broad classification nearly two hundred and the individual installations may be counted in the thousands



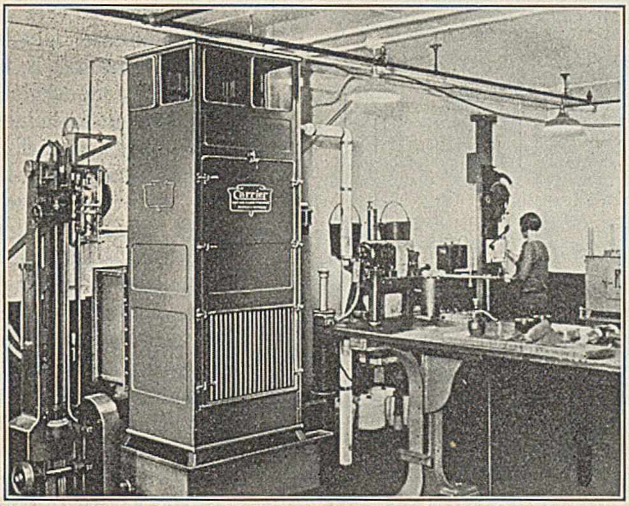
Controlled Atmospheric Drying and Processing of Tobacco. Bayuk Cigars, Inc.

Subjection of Shoe Uppers to Conditioned Air Prior to Stretching on Lasts. International Shoe Company

Air conditioning—the automatic control, establishment, and maintenance of conditions of temperature, humidity, air movement, and air purity—is applied broadly for three purposes. Hundreds of materials in the process of manufacture must at some stage be dried or have water or other liquid removed by evaporation. The reverse of this is occasionally demanded. It is frequently necessary or desirable to subject materials to a moist atmosphere for the purpose of absorbing water either to make it more workable or to bring it to some standard weight for test or sale.

Then there are numerous manufacturing operations in which the quality of the final material or the efficiency of the operation, or both, is highly sensitive and variable to the atmospheric conditions. Now it is possible to create and control the conditions best suited to all phases of the operation.

Finally, air conditioning is applied to create and control atmospheric conditions best suited to the health, comfort, and efficiency of people within doors, and the advantages of air conditioning applied primarily to control a manufacturing operation have frequently proved an incidental benefit and profit of even greater importance in their effect upon the health and efficiency of the workers.



Unit Air Conditioner in Fisk Rubber Company Laboratory, Where All Standardized Tests for Tire Fabrics and Rubber Are Made under Constant Temperature and Humidity

Air Conditioning for Drying and Processing of Materials

Drying, as the word is commonly used in many industries, most frequently implies processing, in that the removal of water or other volatiles from materials is always accompanied by physical, and often by chemical changes which influence the character of the product.

The most important consideration in determining the effect of drying or processing upon the final characteristics of material is the rate of moisture removal during the various stages. The control of this rate introduces the necessity for controlled atmospheric humidity, controlled temperature, controlled air movement—in other words, air conditioning. The old, and not yet entirely abandoned, methods of drying were wasteful. Slow drying in the normal atmosphere most frequently means the standing of large quantities of material representing a great investment, occupying large floor areas, and hampering the efficiency of successive operations. The earlier attempts at the forced circulation of heated air over materials resulted in an appreciable loss through breakage and spoilage caused by uncontrolled evaporation.

We now have an understanding of evaporation, and to the manufacturer air-conditioned driers are available which automatically control and vary the conditions of temperature and humidity according to a predetermined schedule, and this in

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[2] *Proc. Am. Soc. Mech. Eng.*, **33** (1911).

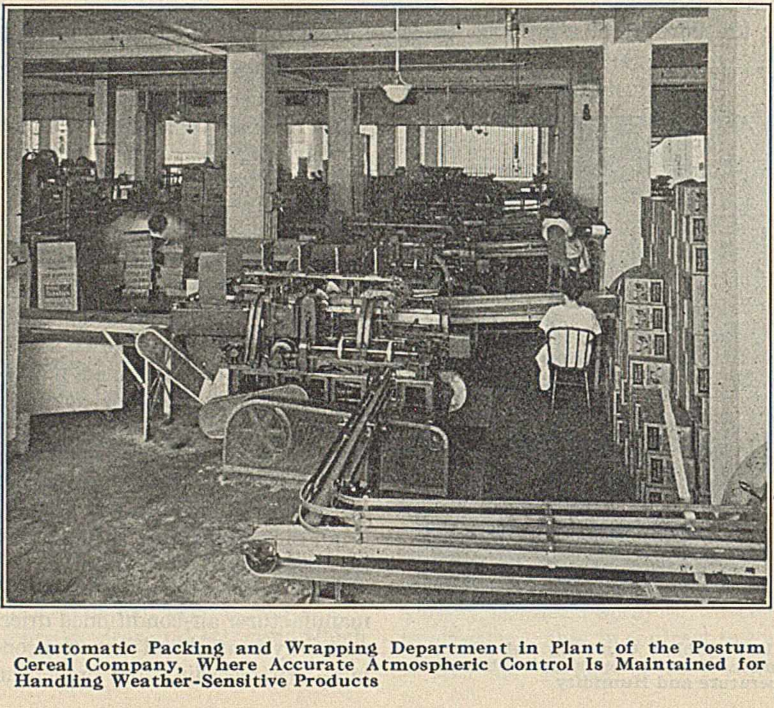
complete independence of weather and seasonal variations. The modern drier meets the schedules of the other manufacturing operations in the plant. Most often the time required for drying is greatly reduced through retarding the rate of evaporation during the early stages only to accelerate it at the proper point when the danger of injury to the material has passed. Most often, too, the modern air-conditioned drier means a great saving in floor space.


Winding Room in Rayon Plant of the American Bemberg Corporation
Conditioned air is distributed throughout the department through diffuser outlets shown in the metal duct near the ceiling.

A manufacturer of sanitary pottery had planned to erect a new building with the purpose of doubling his production. The proposed investment involved a sum of nearly $200,000. An installation of modern drying equipment in his plant, involving an investment of $25,000, speeded up his schedule and liberated enough floor space so that his production of finished material was doubled without following his original plan for building expansion.

A Pacific coast manufacturer of roofing tile, by the installation of modern drying equipment, reduced his drier breakage from an average of 8 per cent to less than 0.25 per cent.

A cigar manufacturer formerly used an entire floor and the labor of twelve men to dry his filler tobacco in a non-controlled but heated room. The installation of a modern insulated drier with ejector air circulation reduced the required floor space to less than one fifth, reduced the labor to the part-time services of eight men employed in the moving of trucks and spreading tobacco on trays, reduced the drying time from an uncertain period of several days to a fixed schedule of 36 hours, and reduced the scrap or tobacco broken from overdried leaves from 20 per cent to less than 2 per cent. Since the installation of these driers this manufacturer has applied air conditioning, drying, and processing systems to every process from the preparation of tobacco to the final packing and storage of cigars in all his factories. He is making more than a million cigars per day.


Automatic Packing and Wrapping Department in Plant of the Postum Cereal Company, Where Accurate Atmospheric Control Is Maintained for Handling Weather-Sensitive Products

In the manufacture of shoes it is highly desirable to moisten or condition the shoe uppers prior to stretching them on the lasts preparatory to soling. A fixed moisture content in the leather and uniform pliability of the upper is quite necessary to the standardization of sizes and to the avoidance of damaged shoes or "seconds." Previous to the installation of a controlled conditioning room the average number of "seconds" per day in a New England shoe factory was twenty-five pairs. Controlled conditioning has virtually eliminated this loss.

Air Conditioning in Manufacturing Operations

The effects of air conditioning as applied in manufacturing operations have been no less remarkable than those in drying and processing. Rates of production have been made uniform, production efficiency has been increased, and the quality of the product improved.

We have remarked that air conditioning, or at least controlled humidification, is quite essential to the modern textile manufacturing methods. Within the last twenty years the world has acquired an absolutely new industry in rayon. Rayon is a textile, to be sure, but its production is chiefly a series of chemical processes. In 1928 more than 110 million pounds of rayon were used in the United States, of which about 98 million pounds were produced within our own shores. Almost from the first process step and up through to the last in this gigantic new industry, air conditioning is an essential factor.

The printer and lithographer are turning to air-conditioning equipment to remedy fickle weather conditions in their effect upon weather-sensitive paper, gelatin rollers, and inks.

The ancient industry of flour milling is becoming modernized. High-speed machinery and large centralized mills are replacing the old countryside grist mill. High-grade flour is being demanded by the public. The weight and moisture content are fixed by government regulation. Standardization is again necessary in order that reputations may be built through a period of years under nationally advertised trade names. Air conditioning has entered this field to cleanse the air coming in contact with the stocks in the flour mill, to maintain the moisture content in the stocks which prove most suitable for efficient and economical milling, and to maintain a final moisture content in the products such that the miller will not suffer from the invisible loss of evaporation. An engineering survey in collaboration with the owners of an air-conditioned flour mill in a southern state, where about 1800 barrels of flour are manufactured each day, showed a tangible saving of $21,000 during the first year on an investment in air-conditioning equipment amounting to $17,000. This saving took no account of the many intangible advantages, among which were the improved health, comfort, and efficiency of the operatives.

Air Conditioners in Flour Mill of J. Allen Smith Company

Non-shatterable glass is becoming standard equipment on automobiles. The lamination of sheets of glass with celluloid is accomplished effectively and efficiently only under the most favorable atmospheric conditions, which are now being maintained in some of the most important factories producing this material.

A relative humidity of 10 per cent and below at temperatures in the neighborhood of 100° F. is being maintained in rooms where telephone toll cables are being wound, in order to maintain the lowest possible moisture content and thus the highest insulating properties in the paper surrounding the fine wires encased in the cable. This condition is not duplicated by out-of-door climate even in the most arid regions of our globe.

Lacquer and other cellulose coatings on fabrics and metals have assumed industrial importance. The evaporation of the volatile solvents used in these coatings introduces evaporative cooling, which frequently causes the condensation of atmospheric moisture on the surface. Trouble follows—blushing, blistering, defective surfaces, and delayed operation. Cooling and dehumidification—air conditioning—are being applied to remedy these difficulties.

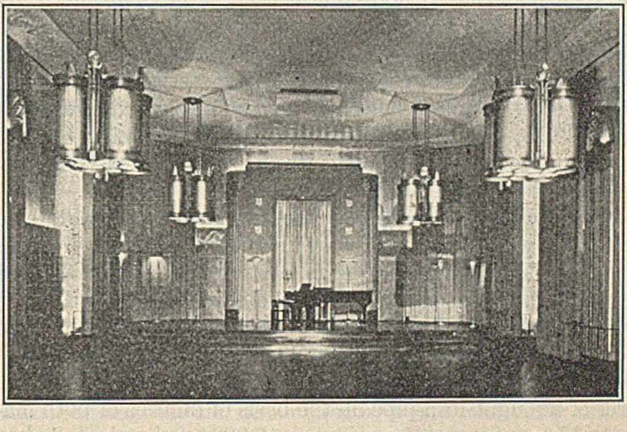
Modern industrial production has ridden forth on the development of automatic machinery. Wherever there are packing, wrapping, and sealing to be done, the automatic machine has largely replaced hand labor, has led to standardization, has improved conditions of sanitation. But where delicate mechanical fingers are involved, wherever hygroscopic materials such as paper, cardboard, and glue are being handled, variable weather conditions cause trouble. Temperature, humidity, and air cleanliness are being controlled by air-conditioning equipment in many modern plants depending upon such machines for their production.

Air Conditioning for Health, Efficiency, and Comfort

When we approach the subject of air conditioning as applied primarily for the comfort, health, and efficiency of people within doors, we are dealing with factors quite intangible in comparison to the actual evaluation upon which we may lay our finger in manufacturing operations. There is little doubt, however, that people who are physically comfortable are more likely to be happy and efficient in their work. We know, too, that perhaps the greatest economic and industrial loss which we experience is through sickness, most often the common cold, accompanied by idleness and wasteful labor turnover. It is only common sense also to say that it is quite as desirable to live in an atmosphere of clean air maintained at conditions of temperature and humidity which are comfortable as it is to drink only pure clean water.

We mentioned previously that many manufacturers have discovered that the air-conditioning system installed primarily to effect a uniform condition for their products has had some remarkable effects upon their employees. Within recent years this understanding of the human relation to atmospheric comfort has grown tremendously and we have no doubt that the application primarily for human comfort within industrial plants and offices has only begun. The public has become mindful of air conditioning through its introduction into many of the large motion-picture theaters in all parts of the country. There are now several office buildings which offer with all offices complete air conditioning; air that is washed, cooled, and dehumidified during the summer, air that is cleansed, warmed, and healthfully humidified during the winter.

Recent developments have made air conditioning for the home a reality. A system is available which cleanses, warms, humidifies, and circulates the air to all parts of the house. Shortly equipment will be available which will add to this system the possibility of cooling and dehumidifying all or a portion of the home during the summer.



One of the Studios of the National Broadcasting Company, New York, a Sound-Proof, Windowless Room in Which Conditions of Comfort Are Maintained for the Performers through a Complete Air-Conditioning System

What air conditioning combined with the kindred fields of illumination, invisible spectrum radiation, and sound insulation will ultimately mean in industry, in the office, in the hotel, the hospital, the department store, the home, requires only a little speculation.

Corrosion—A Problem in Protective Coatings[1]

F. N. Speller

NATIONAL TUBE COMPANY, PITTSBURGH, PA.

THE large and increasing tonnage of metals subject to corrosion in the industries has brought the question of conservation to the front as a major engineering problem. In pipe lines, tanks, and oil refineries, for example, a recent census shows that losses and cost of maintenance amount to more than one hundred million dollars a year in the oil industry alone. In modern cracking stills ordinary steel tubes often last only three or four months. Prevention of corrosion may be worked out along three lines: by developing more resistant metals, by reducing the corrosive character of the environment, or by the use of more stable protective layers of materials which are cheaper and much more resistant than the metal.

Twenty years ago the prevailing opinion was that the rate of corrosion of metals, like their common physical properties, depended mainly on certain inherent characteristics. While it is probably true that in some cases the solution pressure or tendency to corrode is very different in different metals—such as platinum and iron to take extreme examples—this does not explain fully the difference in rate of corrosion of different kinds of iron, aluminum, brass, and other of the more common and less durable metals. For the immediate discussion let us confine our attention to the various well-known ferrous alloys. As a result of experience it is now generally conceded that the *rates* of attack of wrought iron, cast iron, and the various forms of ordinary steel in soil and water are, as a rule, but little different; in the atmosphere more variation is found in these metals.

Relative Corrosion of Wrought Iron, Steel, and Pure Iron

It is surprising how much has been taken for granted without any real evidence on the question of the relative merits of wrought iron, steel, and pure iron. A little frank discussion of the facts of the case may not be out of place at this time.

Large investments are now being made in low-cost methods of making so-called wrought iron by mixing molten cinder with hot steel particles without the use of the labor formerly required in the old hand-puddling process. Before using synthetic wrought iron on a large scale, it would seem advisable to determine whether the old iron was materially better than modern steel, as some claim it to be, and also whether the new iron made by radically different methods is as good as the old. The evidence from comparative tests is certainly not convincing as to the alleged superiority of the older material. However, widespread advertising has founded and maintained industries where the public are unable to check the claims readily. For example, a large eastern gas company used wrought iron from 1898 to 1906 and steel pipe from 1906 to 1916. They published the number of services which failed each year during this period with respect to the time in service.[2] These data were charted and published by a manufacturer of wrought-iron pipe on the basis of failures of both materials, for each year of service per 10,000 services installed.

The method of presenting these data leads to the conclusion that after several years the steel corrodes four or five times as rapidly as the iron. This method of comparison ignores the fact that the pipes were laid at different periods and in different localities. It is well known that soil conditions vary considerably in large cities, but the fact that this company is still using steel pipe exclusively indicates the erroneous nature of this comparison. Their real conclusion from this experience and tests is "that there was very little difference in the corrosive effect of soils on wrought-iron and steel pipe,"—very different from the one expressed in the report of these tests as issued by the wrought-iron interests.

Figure 1 gives another analysis of these data accepted by the gas company and based on the probable average life of services for each year of installation where sufficient data are available. This was obtained by estimating by probability curve calculations the average life of the services installed in each year from 1898 to 1914[3] from the failures recorded for each year. The failures to date of steel pipe installed after 1914 are too few to give an accurate estimate. It will be seen from this figure that the wrought-iron pipe installed prior to 1903 shows a somewhat longer life than steel, after this date there is very little difference. This has been explained by the fact that previous to 1903 most of the services were laid in virgin soil, whereas after that time as the city limits were extended most of the services were placed in filled ground.

It is significant to note that the United States Bureau of Standards soil tests indicate no material difference between wrought-iron, copper, steel, and other kinds of commercial steel pipe in many typical soils, in various parts of this country. The variable factors in soil corrosion are more numerous and harder to control than in water or air, so that the agreement of the general averages of these two sets of data, one from actual experience and the other from measured corrosion in a wide variety of soils, is significant. Most of the large gas and oil companies which use thousands of miles of line pipe, have come to the conclusion that there is practically no difference between these materials.

Corrosion and Electrochemical Theory

Early investigations by the writer indicated that ordinary segregation of foreign materials in steel had no influence in controlling the location of the areas attacked (anodic areas), but that the external potential, such as that induced by relatively large areas of mill scale, was sufficient to direct and maintain the attack on certain anodic areas and cause in time perforation of the metal.

Before considering certain preventive measures, it may be well to state briefly the principle of the electrochemical theory of corrosion which is now generally accepted in explanation of the initial corrosive attack at normal temperature. At high temperatures and occasionally at temperatures not far above normal, direct chemical attack may occur. The initial reactions when metal is first exposed to water and oxygen are:

$$\begin{array}{lll} \text{I} & \text{M (metal)} + 2\text{H}^{+}\text{(ionic)} & = \text{M}^{++}\text{ (ionic)} + 2\text{H (atomic)} \\ \text{II } (a) & 2\text{H (atomic)} + {}^{1}/_{2}\text{O}_2 & = \text{H}_2\text{O} \\ \quad\ (b) & 2\text{H (atomic)} & = \text{H}_2\text{ (molecular)} \end{array}$$

As a result of these reactions the solution tends to become alkaline at cathodic areas and acid at the anodes. Most metals when first exposed to water show initially a high rate of solution, which quickly slows down as the polarizing film of

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[1] Presented before the Montreal Chapter of the American Society for Steel Treating, January 14, 1929.

[2] *Proc. Am. Gas Assocn.*, **6**, 1234 (1924); supplemented by data in later reports of American Gas Association Distribution Committee.

[3] Kendall, *Am. Gas Assocn. Monthly*, **10**, 493 (1928).

hydrogen forms on cathodic areas, and the reaction can only continue by removal of the atomic hydrogen film either by combination with free oxygen or as hydrogen gas.

In case corrosion products are insoluble, surface films form which greatly retard and sometimes stop the reaction. The metal surface may thus become completely covered with a film of corrosion products ranging in thickness from an atomic layer to one of measurable dimensions. These films may form on anodic or cathodic areas. After a film forms over an anodic area, the potential may be reversed, and this change of potential may occur repeatedly, resulting in fairly uniform corrosion.

Ordinary corrosion is dependent upon the maintenance of a supply of free oxygen and water at the metal surface and is influenced largely by temperature, rate of motion, hydrogen-ion concentration, local changes in potential due to oxygen concentration cells or dissimilar metals in contact, protective films, and many other variables. The retardation of corrosion is most generally brought about, however, by the formation of more or less impermeable protective films on anodic areas. These films start to form shortly after the metal comes into contact with a corroding solution. They consist essentially of the products of corrosion and attain their maximum protective power after a certain period of time. This may be looked upon as a self-healing property possessed by some metals without which they would have a considerably higher rate of deterioration and be much less useful. It should be our aim to cultivate this valuable property in metals. In fact, it seems to the writer that metals having high corrosion resistance may be better developed by a scientific study of the stability and formation of surface films than by the old cut-and-try method of making and testing the effects of various alloying elements. Some work has already been done on the study of the electrical resistance of these films, but more knowledge of the initial rate of attack and the rate at which corrosion is retarded by the alloying of certain elements with iron should be helpful in explaining the mechanism of the resistance to corrosion.

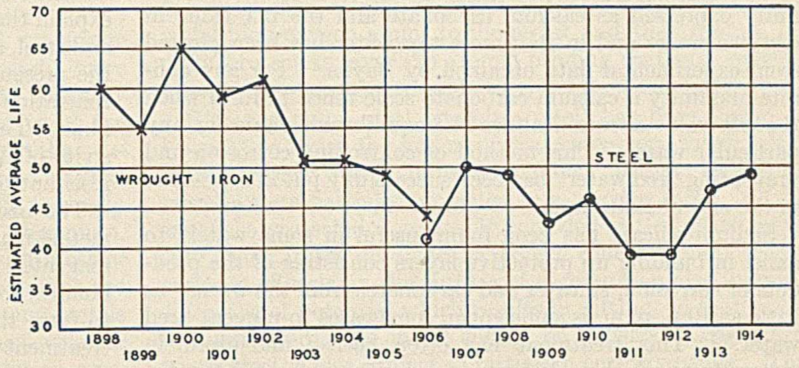

Figure 1

When clean iron, aluminum, zinc, and many other metals are exposed in a corroding medium (either in a solution or a gas at ordinary or higher temperatures), the rate of attack is usually rapid at first and slows down quickly in a short time to a lesser rate, which may be comparatively uniform unless there is some change in the corroding medium. The rate of attack is retarded at a rate depending upon the capacity of the metal to form a self-protecting film, which is very rapid in the case of such metals as high-chrome iron and aluminum, and much slower with other metals, depending in all cases very much on the corroding reagents and the nature of the products of corrosion. This is a very significant observation, which requires much more experimental work before it can be stated as a law in more precise terms, but it can be confidently said at present, based on a large amount of experimental evidence, that external influences predominate in controlling the corrosion rate of any metal. This being true, it is important to understand the various ways in which the rate of attack is governed by changes in external conditions, including the surface films that naturally form on a metal surface and tend to re-form when broken by a self-healing process.

Natural Protective Films

For lack of space the subject of deaeration and other means by which corroding media may be rendered much less active will be passed over here, except that it should be noted that such means are sometimes more economical than other preventive measures.

A few examples of protection of metals by building up natural protective films will now be considered.

A natural protective skin is often formed under atmospheric condition at normal temperature. In 1909 the writer reported a study of old French iron and steel on the Panama Canal site.[4] Some of this old material was thoroughly protected by an adherent oxide but showed no evidence of painting. However, when the surface skin was machined off and the clean metal was exposed with modern steel similarly prepared, they both corroded rapidly at about the same rate. Evidently the initial cycle of weather conditions (wetting and hot-drying) has much to do with the ultimate life of the metal, depending upon whether or not a stable protective film is formed.

Evans[5] reports an investigation which he made on some old galvanized-iron roofing sheets which had resisted exposure to sea spray in the Scilly Islands successfully for fifteen years. He showed definitely that the older material was more resistant than new galvanized sheets and that this was due, not to any essential superiority in the older zinc coating, but to a permanent protective film that had evidently been acquired during the initial period of exposure. There is considerable evidence like this pointing to the fact that the conditions prevailing when the metal is first exposed, such as the physical character and adherence of the early products of corrosion, have considerable influence on the subsequent life of the metal.

Evans[5] artificially produced a protective film on a zinc-coated steel surface by alternately spraying with 0.01 *N* sulfuric acid or 0.5 *N* sodium chloride and drying, which increased the resistance of the metal when later immersed in 0.5 *N* sodium chloride.

Certain inhibitors reduce the rate of solution of metals in acid solutions. It has been shown that this is due to an increase in the hydrogen overvoltage which is generally assumed to be due to formation of a film of discharged inhibitor substances adsorbed on the cathodic areas. The theory of inhibitor action has been well stated by one group of investigators as follows:[6]

> When immersed in acid, iron goes into solution at the anode areas, forming ions and discharging hydrogen ions at the cathode areas. These cathode areas may be said to occur principally in the narrow spaces of the grain boundaries in steel or between the metal and slag in wrought iron. Most inhibitors are either bases, such as quinoline, or positively charged colloids, and when these are present they travel to the cathode areas with

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[4] Speller, *Proc. Am. Soc. Testing Materials*, **9**, 440 (1909).

[5] Evans, "Corrosion at Discontinuities in Metallic Protective Coatings," presented at Institute of Metals, Liverpool, England, September, 1928.

[6] Chappell, Roetheli, and McCarthy, IND. ENG. CHEM., **20**, 596 (1928).

> the hydrogen. When the positively charged heavy particles are discharged, they cannot escape by gaseous evolution, and accordingly are adsorbed on the surface, building up a protective layer.

Another well-known example of film protection is found in the action of alkalies in solution. Some work done a few years ago by the writer and one of his associates[7] indicated that the initial rate of corrosion of iron in water having various concentrations of caustic soda did not vary materially, but that several minutes later the corrosion rate had decreased to a fixed minimum depending upon the hydroxyl concentration. This is explained by the lower solubility of ferrous hydroxide in the more alkaline solutions.

The relationship between the equilibrium values for alkalinity expressed as calcium carbonate and the pH value in distilled water and in Baltimore tap water has been plotted from experimental data obtained by Baylis.[8] For any definite alkalinity a calcium carbonate scale tends to form when the pH value is raised above the equilibrium value for any particular water. This method of controlling corrosion and preventing "red water" has been successfully put into practice in the city of Baltimore.

Sodium silicate has been found useful in some waters to assist in building up protective layers consisting of the products of corrosion, silicates and carbonates from the water; as little as 10 p. p. m. is sufficient in some cases to prevent "red water."[9] This treatment has often been found useful in waters from which scale-forming constituents have been displaced by the zeolite process. The solution of lead may be stopped by the use of a small amount of soluble silicate in the same way. Silicate layers build up slowly and break down after a certain period of time, when the water treatment is discontinued.

May and Carpenter[10] give some interesting examples of the building up and repair of broken surface films on non-ferrous condenser tubes and trace the formation of these films by a series of measurements of the film potential.

Passivity is induced in iron and ferrous alloys, zinc, aluminum, copper, and other metals when they are subjected to the action of strong oxidizing reagents such as strong nitric acid, chromic acid, or a rather strong solution of chromates.[11] A metal may also be rendered passive to corroding reagents by anodic attack. To form such a film the voltage must be sufficiently high to cause evolution of oxygen at the anode.

So long as a certain low concentration of the passivifying reagent is in contact with metal, it is kept immune from attack under the action of corrosive solutions, even with alternating stresses that in the absence of the inhibitor would cause rapid destruction of the metal. McAdam[12] has shown that the endurance limit of iron and some other corrodible metals is greatly reduced by the combined action of cyclic stresses and corrosion produced by a stream of water impinging on the stressed specimen. The present writer and his co-workers have shown that 200 p. p. m. of sodium chromate in ordinary tap water will completely overcome this effect, evidently by maintaining the passive film.[13] In reporting their experiments on cyclic stress and corrosion, particular attention was called to the fact that a narrow band of lacquer or loose rubber surrounding the test piece caused failure, evidently due to a localized acceleration of corrosion, which was sufficient to overcome the passivifying effect of the inhibitor, which otherwise gave good protection under the same stress.

All these observations and experiments indicate that passivity is due to invisible film protection. Evans[14] showed that some of these invisible passive films may be raised off the metal surface and rendered visible.

It is not surprising that these very resistant films are so thin as to be invisible, as corrosion under these conditions is quickly arrested and the growth of the film must then cease. Evans[14] has shown that oxygen uniformly distributed over the surface of a metal in water tends to passivify iron. This may explain the abnormal resistance occasionally found in old iron and steel, and zinc-coated iron and steel. On the other hand, the present writer has found that variations in oxygen concentration have a marked tendency to break down protective films. There is therefore good ground for considering passivity of all kinds, including the slow corrosion of special steels resistant to corrosion, as due to film protection.

The accelerating influence of contact between dissimilar metals may be offset more or less by the use of passivifying reagents. To passivify metals, in practice, it is most economical to use sodium dichromate with sufficient caustic soda to form the normal chromate. The writer has applied this treatment to stop corrosion in water cooling systems where the water is recirculated over and over. About 200 p. p. m. of the dichromate are usually sufficient, although the amount required varies with the composition of the water, particularly its chloride content. This treatment is also useful in retarding the action of refrigerating brines on plain and galvanized steel. A 20 per cent brine requires 1500 p. p. m. of dichromate and 400 p. p. m. sodium hydroxide. Naturally the surface film is harder to maintain in high-chloride solutions, but practical experience for more than a year at several ice plants has demonstrated the value of this treatment by which the corrosion of equipment is reduced by 80 per cent.[15]

Protection with Thick Coatings

Thick coatings of more or less inert material are often applied economically to protect the more expensive steel construction such as underground pipe. As a rule, paints are hardly worth the expense of application, except where exposure is to the atmosphere.

In this class of protection we have Portland cement, concrete, and reënforced bituminous coatings. Cement-lined pipe and fittings are now available for water service at ordinary temperature in all the common sizes. The coating is applied by centrifugal action for the larger sizes and by drawing a mandrel through the pipe for the smaller sizes. Neat cement with 25 per cent fine sharp sand is usually employed. For a few months the water passing through cement-lined pipe will be slightly harder and more alkaline, but as the free lime becomes leached out this effect disappears. In New England fifty or sixty years of service have been obtained from cement-lined water pipe.

A new process (Talbot) of centrifugally lining water mains with an asphalt mastic (70 per cent sand and 30 per cent asphalt) has been developed in England and plant for lining up to 30-inch pipe has been erected by the National Tube Company in the United States. This gives a very durable coating but is somewhat more expensive than cement. Enamel- and rubber-lined pipe are also available for special purposes.

The protection of pipe lines from soil corrosion is being

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[7] Speller and Texter, Ind. Eng. Chem., **16**, 393 (1924).

[8] Baylis, *Am. Water Works Assocn.*, **15**, 598 (1926).

[9] Speller, "Corrosion—Causes and Prevention," p. 350, McGraw-Hill Book Co., 1926.

[10] May and Carpenter, "The Corrosion of Condenser Tubes," presented at Institute of Metals, Liverpool, England, September, 1928.

[11] E. L. Chappell, of our Research Department, has shown that hot-dipped zinc-coated pipe, when quenched in water carrying a small amount of chromate, is much more resistant to corrosion than when the chromate is not added.

[12] McAdam, *Proc. Am. Soc. Testing Materials*, (preprint) **41**, 29 pp., June, 1928.

[13] Speller, McCorkle, Mumma, *Ibid.*, *Reprint* No. 42, 9 pp., June, 1928.

[14] Evans, *J. Chem. Soc.*, **1927**, 1020.

[15] *Refrigerating Eng.*, **12**, 22 (July, 1928).

studied in detail by representatives of the American Petroleum Institute and the American Gas Association. Thick bituminous coatings are generally used, frequently reënforced with saturated fabric to hold the bitumen on the metal. The Petroleum Institute's corrosion committee has recently issued a tentative code of good practice for the coating of pipe.[16]

More Resistant Metals

Having considered a few examples of unstable metals which may be made less corrodible by the formation of a protective layer on the metal surface without any change in the metal itself or by application of protective coating, let us now consider what can be done towards prolonging the life of the metal by alloying it with other metals.

When the electrolytic theory was first discussed, some were led to the conclusion that a high degree of purity and a more homogeneous structure would give longer life to ordinary steel. Greater purity of the metal has not proved to be the answer except under acid attack. We now know that external factors usually control the rate of corrosion and that all commercial grades of iron are much alike in being naturally more corrodible under some conditions than chromium, nickel, or copper. Fortunately, iron can alloy with most of these more resistant metals, forming solid solutions that are in many cases much more resistant than the alloying metals themselves. The essential characteristics of a rust-resisting metal are apparently that it would have a low solution pressure and form impermeable, tenacious, and stable surface films in combination with corroding media. These films should be, and usually are, much more stable than the metals which enter into their structure, but as they are attacked differently under different conditions, it is not to be expected that a metal will soon be found that is equally resistant under all conditions. Gold and platinum are at present the only metals that are resistant to nearly all corroding reagents.

Let us take the case of steel with the addition of 0.25 per cent of copper, which is now well established commercially. Long-time exposure tests in service have shown an increased life of from two to four times in atmosphere by the addition of this amount of copper to ordinary Bessemer steel, whereas the same steel under water or in corrosive soil is apparently no better than ordinary steel without copper. In the former case, when the metal first goes into solution, copper is precipitated *in situ* and a double oxide of copper and iron is formed. In water, on the other hand, the rust is loosely formed and less dense, suggesting that the small amount of copper is carried away from the corroding surface when the metal dissolves and therefore plays no part in the formation of a protective layer. It is a curious fact that copper forms a denser film on the more impure forms of steel, so that copper-bearing Bessemer steel is more resistant in certain atmospheres than open-hearth steel or commercially pure iron with the same copper content.

For most purposes where large tonnages of metals are involved, the world is interested in the use of iron as a base for a more durable metal having useful physical properties. Small additions (1 or 2 per cent) of chromium, nickel, or silicon to iron have not given encouraging results, under ordinary corrosion, but when the amount of chromium or silicon exceeds 12 or 14 per cent a very marked stability is produced, particularly under atmospheric exposure or where the metal is exposed to strong oxidizing conditions. This amount of chromium in solid solution in iron forms a very resistant oxide film which is self-healing except under those conditions where the film is destroyed, as in the presence of an excess of chlorides. High-chromium iron when immersed in copper chloride solution after careful cleaning in the absence of oxygen goes into solution and precipitates copper like ordinary iron. The addition of 8 per cent or more of nickel still further increases the stability of the surface film under a wider range of conditions. An attractive field of research is open in the study of the stability of films made up of combinations of oxides. More fundamental information is also desirable on the initial rate of corrosion of these alloys, which appears to depend upon the type of anodic film protection produced in the corroding medium.

These are fundamental problems worthy of the close attention of physical chemists. The nature of the bond which holds these passive films on the metal is also an interesting field of speculation. It may be, as Guertler[17] points out, that the unsatisfied attractive bonds of the surface atoms of the metal bind oxygen atoms to the metal and thus form a primary protective layer (an atomic priming coat as it were) to which a more protective oxide layer is often attached.

High-chromium steel (stainless steel) has been shown by Friend[18] to resist the action of sea water very much better than ordinary steel similarly exposed, except where the samples were partially protected in a wooden rack. All the metals so protected were deeply corroded at that place, probably owing to the difference in oxygen concentration. Small particles of scale on the surface of chrome iron also induce a difference of potential which results in pitting, so that to get the best results the metal should be polished. High-chromium steel is also subject to pitting in corrosive soils. This and other circumstantial evidence, as pointed out before in this paper, leads to the conclusion that the superior resistance of such steels is due to the surface film formed rather than to any great reduction in the solution pressure of the metal by the chromium addition. As the life of the steel is so materially influenced by small variations in surface potential, the surface film hypothesis seems highly probable.

All this being true, it follows that to improve the durability of iron, the compounds of iron and other metals that are most resistant under certain conditions of service should first be investigated, and then the most likely ones selected in an endeavor to form solid solutions of iron and other metals that will form these resistant films when the metal corrodes. The chief alloying metals available in practice are copper, nickel, chromium, silicon, and aluminum. Since double compounds of these metals are as a rule more stable, a research of this kind is likely to take some time and patience. However, much has already been learned by experience and useful alloys of iron, chromium, and nickel are now available for various purposes where first cost is of secondary importance. A low-priced alloy is needed which will be two or three times as durable as ordinary iron in air, soil, or natural waters without much additional cost. Experience with the iron-chromium, iron-nickel, and iron-silicon series points to the necessity of a large amount (over 13 per cent) of these alloying metals in solid solution and does not offer much promise of the early development of a low-cost rust-resisting iron alloy.

Aluminum is an example of a metal that quickly forms a stable oxide film and on this account possesses high resistance to atmospheric corrosion. In contact with chloride solutions this film is soon penetrated and destroyed, and, in consequence, under these conditions the metal has a comparatively short life. Aluminum in considerable amounts (perhaps with other metals) may prove to be a useful alloying agent in iron for certain kinds of exposure.

Variations in water, local differences in surface potential, and other factors may affect the stability of the film formed on metals, so that tests should be made under service conditions or by using the same controlling factors that are found in

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[16] *Proc. Am. Petroleum Inst.*, December, 1928.

[17] Guertler, *Trans. Am. Soc. Steel Treating*, **13**, 759 (1928).

[18] Friend, *Carnegie Scholarship Mem.*, **16**, 131 (1927).

practice. Too often the impatient investigator resorts to an acid test and misleading statements are prematurely published which tend to discredit other work. Popular advertising of special alloys of iron with a dash of this or that and a cryptic name should be viewed with suspicion until satisfactory tests under specific conditions of service are obtained. Thus far no low-priced iron alloy has been put on the market that seems worth the difference in cost except for atmospheric exposure, and ordinary Bessemer steel with a little copper seems to be at least as durable as any other for that type of service.

Conclusions

1—Corrosion is determined and controlled by influences external to the metal which either form or destroy surface films on the metal.

2—Protective films form more readily in air than in water or soil.

3—Where the metal is continuously in contact with soil or water, commercial steel or wrought iron suffers about the same under the same conditions of exposure irrespective of method of manufacture or the amount of foreign material present, within wide limits.

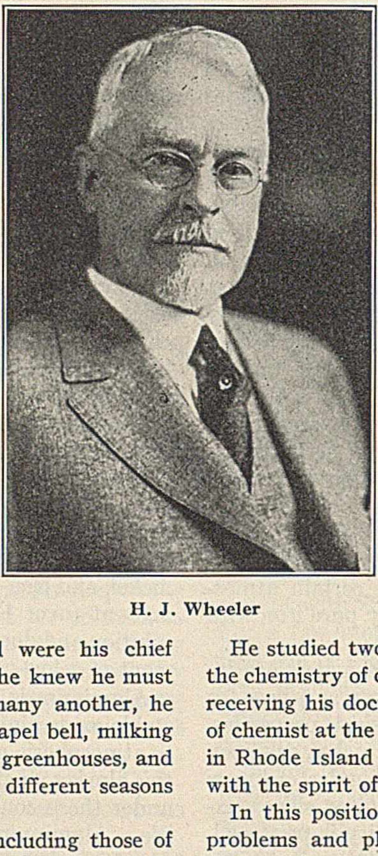
4—When exposed in air, however, copper in amounts over 0.15 per cent has a marked effect in forming a stable surface coating of oxides which increases the life of the metal at least two or three times. This is the result of tests in service extending over a period of more than ten years. There is no such evidence as yet that other additions give additional life.

5—For highly corrosive conditions where the first cost of metal is not of prime importance, suitable metals are now available, such as the 18 per cent chromium-8 per cent nickel alloy, but in selecting the most economical alloy for any particular purpose it is important first to study the environment and select a metal that contains the elements that will be most likely to form a stable surface film under conditions of service.

AMERICAN CONTEMPORARIES

Homer J. Wheeler

THE truism that "we build the ladder by which we rise" finds striking exemplification in the subject of this sketch. While ultimately this structure is an individual product, the reliance on individual initiative and resources in the early stages of its building may vary widely. Some have the timber for it selected and furnished them with little effort; others have encouragement and material help in framing the lower rungs and getting the structure well under way; but as it rears in height it reflects the measure of the man. Homer J. Wheeler began at the bottom, and supplied the moral and intellectual fiber for his rise.



H. J. Wheeler

Reared on a farm in Berlin, Mass., he made the most of the local school opportunities and became imbued with a desire for a college education which would give him a larger intellectual outlook and opportunity, regardless of what his future vocation should be. When he set out for the Massachusetts Agricultural College in 1879, this ambition and an indomitable will were his chief assets, for he had scant financial support and he knew he must depend mainly on his own efforts. So, like many another, he worked his way through college, ringing the chapel bell, milking at the barns morning and night, helping in the greenhouses, and doing such other work as the farm afforded at different seasons of the year.

It was a stiff pace with many hardships, including those of boarding himself, but he stuck to it through the four years. He was a good student but not a "grind," and he found time to take his part in the student activities. He graduated second in his class, a credit to himself and an inspiration to others who profited by his courageous example.

In his college course he had come under the influence of Charles A. Goessmann, professor of chemistry and a former pupil of Wöhler. Goessmann had long been carrying on agricultural experiments and investigations with meager resources, and working for the establishment of an experiment station. Shortly before Wheeler graduated, such a station was authorized by the Legislature and a small appropriation provided. Wheeler became one of the assistants in the chemical laboratory, and served in this capacity for four years. During that time he continued his chemical studies under the direction of Goessmann, acquiring a vision of the exact and painstaking German methods of scientific research and a desire for a university course. But his meager salary had permitted him to save only a small part of the required funds, and so in his predicament he turned to a member of the board of trustees for a loan. This was granted when the only security he could offer was his high character and an insurance policy on his life. But Wheeler proved a good risk, and his benefactor must have felt proud of his part in aiding this worthy effort.

He studied two years at Göttingen, working under Tollens on the chemistry of carbohydrates and under von Koenen in geology, receiving his doctor's degree in 1889. Fortunately the position of chemist at the newly organized agricultural experiment station in Rhode Island awaited him on his return, for he was imbued with the spirit of research and anxious to get to work.

In this position he entered with zeal upon the study of soil problems and plant nutrition, soon establishing himself as a leader. He instituted a system of laboratory, pot, and field experiments which in connection with chemical studies resulted in outstanding contributions to the knowledge of soil fertility, notably the nature, cause, and cure of so-called acid soils, which he showed to be widespread in this country, and the effect of one crop on another in rotation. He studied intimately the action of various fertilizing materials, the nutritive requirements of plants and methods of determining these needs, sodium salts and their functions in soils and plants, the relations of lime and magnesia to plant growth, and the effect of the soil reaction on various crops and on the prevalence of such diseases as potato scab. In that connection he contributed to the differentiation of acid-tolerant crops from those unsuited to acid soils and showed the relation of soil treatment to acidity. He was the first to note the effect of sulfate of ammonia in increasing the acidity of soils deficient in lime.

Wheeler had the courage to doubt some of the things long accepted as true, and the discernment to devise and carry through studies which he could interpret understandingly. His work was his hobby. He took it seriously and threw his intense nature into it. He concentrated on a few lines and stuck to them. Succeeding pieces of investigation were obvious parts of a whole—the development of a plan or the following up of suggestions that came from his results. The broad, fundamental character of his research was due to this fine quality of concentration, close observation, and constructive thinking. It was this that served to make a relatively small station a conspicuous leader in its field, and give it international reputation.

In his twenty-three years' connection with the Rhode Island Experiment Station, Doctor Wheeler rose to the position of director in 1901, was professor of agricultural chemistry and of geology in the Rhode Island State College, and at one period was acting president. He was prominent in the college faculty and in the agricultural affairs of the state, and held important positions in leading scientific bodies. However busily occupied, he always found time to give sympathetic counsel to a student or an inquiring farmer who sought his help. He maintained close contact with the farmers, and was in demand in other states for addresses in his special field. For what he knew he was able to impart clearly, and his word carried conviction. He never was happier or more at home than when he was discussing with farmers their particular problems and explaining the applications of his findings.

But through it all he has found time for diversion. He loves human intercourse, and he never has lost his love of play. In his younger days he was a good tennis player. Later his dog and his gun were his great diversion. He was fond of boating and of anything that led him out into Nature's playground. When he took up golf it was with the enthusiasm of youth, and it is one of the things which keeps him young.

In 1912 Doctor Wheeler was offered the position of manager of the Agricultural Service Bureau of the American Agricultural Chemical Company, which he has occupied ever since, with credit to himself and profit to his organization. He carried into his industrial position the spirit and the ethics of science, exemplifying the same high type of student and investigator that he earlier did and keeping in close touch with the progress of scientific investigation in agriculture. These traits have preserved his recognition in the organizations he was so long associated with, and accorded him a position of honor. He is a fine example of the scholar in industry.

A forceful speaker and writer, with a charming personality, kind, big-hearted, and generous, he has left a strong impress on a wide circle of younger men and made lifelong friendships. He has led a fine, fruitful life, full of work and full of pleasure, for his work is his greatest satisfaction. E. W. Allen

NOTES AND CORRESPONDENCE

"Stability of Metals at Elevated Temperatures"

Editor of Industrial and Engineering Chemistry:

My attention has been called to the review by H. J. French [Ind. Eng. Chem., 21, 193 (1929)] of the bulletin by Clark and White entitled, "The Stability of Metals at Elevated Temperatures."

The reviewer criticizes the authors for not including stress-strain curves. In fact, he devotes one entire paragraph to this criticism. Possibly a mistake was made in not including at least one stress-strain curve, though we have stress-strain curves for every one of the tests on which we obtained proportional-limit values, and these are available for persons who care to examine them. This particular type of criticism seems to be an obsession with this particular reviewer, in view of the fact that this is not the first time he has made such a criticism.

Again, the reviewer criticizes the authors for failing to furnish supporting evidence with regard to their theories advanced to explain the difference in stability of various metals and alloys. We quite agree that this phase of the bulletin can be developed further, though in some cases it may be several years before proper supporting evidence is advanced. If it should take the trend that our iron-carbon equilibrium diagram has taken, or that our various theories with respect to hardness have taken, it may be many, many years before full evidence with regard to these theories can be advanced, for even yet there is no one generally accepted iron-carbon equilibrium diagram nor no one generally accepted hardness theory. The theories advanced for stability should be viewed from the standpoint of theories as an attempt to develop a rational explanation of stability, and the authors should not be criticized for their failure to support all of their contentions with absolute evidence.

The reviewer objects to the expansion tests, apparently on the basis that they are not accurate. We recognize that creep tests on straight bars of metal as performed in some one or more of the customary manners may be slightly more accurate than expansion tests, though we were ourselves surprised at the closeness with which our expansion tests and the creep values as obtained by reputable investigators coincide. Likewise, the expansion tests were undertaken with the purpose in mind of doing work which we felt would be of application to central stations, for practically all of the material used for high-temperature purposes is of tubular section and we desired, therefore, to find the characteristics of this type of stock without having to go through the transpositions that would be necessary if we used straight stock.

The reviewer has absolutely overlooked the mathematical relationship which was developed between stress, temperature, deformation, and time. We feel this is a very valuable contribution. In fact, it is the first attempt made to put on a rational mathematical basis the relationships in question. Further, he has made no comments about the theories beyond the fact that they were not supported with proper evidence. So far as we know, this is the first time any theories have been advanced, and we felt, and still feel, that it is wise to advance theories, even in the absence of convincing evidence, as it gives an opportunity for all the investigators in the field to carry on work, if they see fit, in accordance with the theories suggested.

The reviewer states that in its present form the book does not add many new facts to current information. This statement is true with respect to certain data, but there is a considerable amount of material to which this statement does not apply. We believe the reviewer has lost the point of view from which the bulletin was prepared—namely, the purpose and intent to place under one cover information and data on this subject that might be of use to the general public, particularly to the users of power-plant equipment. We feel that if we should take the stand that no material except that which includes only new facts should be published there would be a material reduction in the technical literature. We are not sure but that such a step would be desirable, though, beyond question, it would materially handicap many engineers and scientists who wish to familiarize themselves with various fields beyond those in which they maintain acute interests. We do feel, however, that the book has added new facts. It has advanced a theory explaining stability of metals at elevated temperatures; it has developed the mathematical relationship between stress, temperature, deformation, and time; and it has given data on a considerable number of new alloys which have not hitherto been recorded except through certain of our own technical publications.

University of Michigan
Ann Arbor, Mich.
February 11, 1929

A. E. White

Ignition Temperature of Carbon Bisulfide—Correction

Editor of Industrial and Engineering Chemistry:

It has been brought to my attention that the work of Masson and Hamilton [Ind. Eng Chem., **19**, 1335 (1927)] was incorrectly quoted in my paper entitled "Auto-Ignition Temperatures of Flammable Liquids," *Ibid.*, **21**, 134 (1929). The value of 343° C. quoted as the ignition temperature of carbon bisulfide is acknowledged to be an error.

Factory Mutual Laboratories
Boston, Mass.
April 1, 1929

N. J. Thompson

BOOK REVIEWS

International Critical Tables of Numerical Data, Physics, Chemistry and Technology—Volume V. Edward W. Washburn, Editor-in-Chief. Prepared under the auspices of the International Research Council and the National Academy of Science by the National Research Council of the United States of America. ix + 470 pages. McGraw-Hill Book Co., Inc., New York, 1929. To be published in 7 volumes. Price, $84 per set on orders per set only; payable at the rate of $12 per volume as issued.

Volume V of International Critical Tables treats the following subjects: viscosity and fluidity; kinetics of physical processes; mechanical equivalent of heat; specific heat; thermal effects accompanying physical and chemical processes; thermal conductivity; radiometry; spectroscopy; photometry; mechanical equivalent of light; photography; and properties of soaps and their aqueous solutions. An index for Volumes I to V is included.

The completeness of the data is somewhat variable; thus, the viscosity data include only a few pure liquids (the remainder to appear in a later volume), but the data on viscosity of solutions, aqueous and non-aqueous, seem quite complete. The thermal data seem to be the most important part of this volume, and appear to be quite up to date, as the reviewer found data published as late as 1929! The full bibliography of absorption spectra of solutions will also be welcomed. A number of short chapters on highly specialized subjects, such as "electrically exploded wires," "pole effect," "emission of light by spark discharges in liquids," contain data not usually included in books of tables, and which will be useful only to the specialist.

Naturally, International Critical Tables becomes increasingly valuable as each new volume appears, and a final index will certainly double the usefulness of the series to the average consultant, since the system of arrangement of data is not always simple to the uninitiated.—Graham Edgar

Photometric Chemical Analysis. Volume II—Nephelometry. By John H. Yoe. With contributions by Hans Kleinmann. xvi + 337 pages. 44 figures. 15 × 23 cm. John Wiley and Sons, Inc., New York, 1929. Price, $4.50.

A novice with regard to a new procedure is confronted with a host of questions as to technic and limits of application. This book has obviously been planned for the novice as well as for one experienced in nephelometry. The contents are outlined in the goal set by the author as follows: (1) to give an accurate account of the development of nephelometry, (2) to present an impartial discussion of the present status of the theory of nephelometry, (3) to give detailed working directions for using a precision nephelometer, (4) to discuss nephelometric research, (5) to give procedures for the determination of a number of inorganic and organic constituents, and (6) to give an accurate and fairly complete survey of the literature on nephelometry.

This book fills a definite place in the literature of rapid and micro methods. It is in the latter field that so much has been accomplished with so little material. The use of such methods has resulted in important contributions to our knowledge, especially of biological processes; nevertheless one stands in awe of the possibilities of error in manipulation. The value of this book is enhanced by the particular appreciation of the possibilities of technical error.—Paul E. Howe

Heat Transmission. By Margaret Fishenden and A. F. Dufton. Department of Scientific and Industrial Research, Building Research, *Special Report* **11**. H. M. Stationery Office, London. Price, 9 d. net.

The report is a well-presented résumé of the present status of our knowledge of the basic factors influencing the rate of heat transmission through walls. A limited amount of data gathered from various sources dealing with thermal resistance of various walls, heat transfer between surfaces, and effect of meteorological conditions on these surface coefficients is presented. The general principles developed are applied to a discussion of heat losses from buildings under natural weather conditions. Further experimental work is being done to gain more systematic information on the effect of meteorological conditions on the rate of heat losses from buildings.—E. C. Lathrop

Conduction of Electricity through Gases. Volume I—General Properties of Ions, Ionization by Heat and Light. By J. J. Thomson and G. P. Thomson. 3rd edition. 491 pages. The Macmillan Company, New York, 1928. Price, $8.50.

Rarely has a book had such a profound stimulating influence on the development of a branch of science as that of the second edition of J. J. Thomson's classical book which appeared in 1906. It not only recorded the progress in this field up to the time of its publication, but it introduced a new point of view into the study of the constitution of matter and the nature of electricity. Great interest is thus attached to the advent of this third edition after an interval of over twenty-two years. The new volume was started by Sir J. J. Thomson about fifteen years ago and was partly in type when the war broke out. The publication of the present edition is the result of the coöperation of his son, G. P. Thomson. It covers in 482 pages the subject matter of the first ten chapters of the second edition, which there occupied 290 pages. All but about 50 pages out of these 290 are retained without change (except terminology—electron for corpuscle, etc.) in the new edition, so that more than half of this edition is new material. The subject of the mobility of ions is brought up to date in a new chapter of 108 pages. Twenty-four pages are devoted to positive ray analysis, including Aston's work on isotopes. Millikan's determination of electronic charge is treated in 10 pages.

The chapter on Ionization by Incandescent Solids is increased from 40 to 61 pages. The great development in this field would seem to warrant more space, but perhaps it is not so pertinent to the subject of the conduction of electricity through gases.

The spirit as well as the form of the book is the same as in the earlier editions. The plan is essentially an application of the classical kinetic theory to the phenomena of gaseous conduction. It is thus natural that no attempt is made to treat the collisions of electrons with atoms or ions from the standpoint of the quantum theory. Ionization potentials are mentioned practically only in one place (page 472) and quanta only in connection with Einstein's photo-electric equation.

The present value of the classical methods is, in general, amply demonstrated by this book, and by the numerous cases where the more rigorous methods of the new mechanics have not yet been, or cannot yet be, applied to the solution of practical problems. The book is thoroughly recommended, not only to those interested in the historical development and the present status of the subject matter, but to those who still desire to have "physical pictures" to aid them in understanding phenomena.—IRVING LANGMUIR

The Discovery of the Rare Gases. BY M. W. TRAVERS. 126 pages. Edward Arnold and Company, London; Longmans, Green and Company, New York, 1928. Price, $6.00.

This book will be welcomed by the chemists of all nations. "The Gases of the Atmosphere," by Ramsay, outlined the history of the discovery of the rare gases, and gave to the world a picture of the work and problems which were successfully surmounted by Ramsay and his assistants. It was impossible, however, for Ramsay himself to put the personal touch into his account that has been possible for Doctor Travers to do in the present volume. Historically this book is of great value and it is full of interesting details that will be greatly appreciated by chemists who desire an intimate account of Ramsay's monumental discoveries.

The author describes the original controversy that existed among chemists as to the relative credit that should be given to Ramsay and Rayleigh in connection with the discovery of argon. As the book is read one marvels at the slowness with which chemists accepted the evidence for the existence of the new element. And one marvels equally at the attempts to cloud this great discovery with a controversy that involved the two scientists who were themselves beyond such petty jealousies. The correspondence between Rayleigh and Ramsay here published shows plainly that each one was keenly interested in seeing that the other obtained full recognition. The present reviewer was at a dinner at University College, London, in 1908, given in honor of the completion of Ramsay's twentieth year as professor at University College. Lord Rayleigh presided and on that occasion went out of his way to give most of the credit of the discovery of argon to Ramsay, and Ramsay in his reply was equally generous to Rayleigh.

Doctor Travers has had the benefit of the files of Ramsay's original correspondence, his notebooks, and other laboratory records, and has taken full advantage of his opportunities. The book is full of reproductions of original drawings and original notes. The whole controversy in connection with metargon is described in a fair and satisfactory manner and the book as a whole is an inspiration to all research workers whether in this particular field or not.

Doctor Travers has been very modest in describing his own connection with Ramsay's work. He deserves the thanks of all chemists for writing this book and he is to be congratulated upon the results.—R. B. MOORE

A Comprehensive Treatise on Inorganic and Theoretical Chemistry. Volume IX—Arsenic, Antimony, Bismuth, Vanadium, Columbium, and Tantalum. BY J. W. MELLOR. 967 pages. Longmans, Green and Company, New York, 1929. Price, $20.00.

This volume marks another milestone in what promises to be one of our most important handbooks in chemistry. These volumes are fittingly dedicated "to the privates in the great army of workers in chemistry," but to bring together the work of these "privates" in a systematic and connected whole is an exceedingly valuable service which increases the value of the work of the privates many fold. The references are comprehensive and were painstakingly worked out. The sections on the history and uses of the elements present interesting reading for all. Indeed, one working on a particular problem will find great profit in reading the sections dealing with the substances with which he is concerned, for it will bring to light many questions and suggestions, as well as questions as to the validity of some of the statements. In fact, it would be exceedingly interesting if some one could put his finger on the statements in our literature which are in error. Perhaps it may come to a point where an army of privates will be needed to ferret out and correct "wrong facts." This process, of course, is going on more or less in the search for new facts and such treatises as the ones being given to us by Professor Mellor are certainly an exceedingly important tool and aid in our investigations. No chemical library is complete without these volumes.—GEORGE A. HULETT

Organic Syntheses. An Annual Publication of Satisfactory Methods for the Preparation of Organic Chemicals. Volume IX. BY JAMES B. CONANT, Editor-in-Chief. vii + 108 pages. John Wiley and Sons, Inc., New York, 1929. Price, $1.75.

The arrangement of subject matter is the same as that employed in the first volume, which consists, in brief, of a detailed statement of the method of procedure for each preparation, followed by notes, after which references to other methods are given. At the end of the volume is a collection of later references to preparations described in preceding volumes, followed by a subject index comprising material from all volumes of the series. It is to be regretted that an author index, which appeared in the sixth, seventh, and eighth volumes, has been omitted from this one.

In the opinion of the reviewer, the chief value of all the volumes of the series is that they contain specific directions, including the precautions necessary to insure successful results, yields to be expected, etc., for the preparation of compounds seldom described in the laboratory guides usually employed in routine course work. These features commend it to the research student, who sometimes finds, upon reference to original papers for methods of preparation of starting material that he needs, that the yield and other necessary information regarding the compound under consideration have not been recorded.

The present volume gives directions for the preparation of twenty-nine compounds. It is printed on good paper, in pleasing type, and seems to be exceptionally free from typographical errors.—L. CHAS. RAIFORD

Données Numériques sur les Colloïdes et l'Adsorption. Extract from Volume VI of Tables Annuelles de Constantes et Données Numériques (1923–1924). Edited by R. AUDUBERT and M. QUINTIN. 56 pages. 22 × 27 cm. Gauthier-Villars et Cie., Paris, 1928. Price, bound, 50 francs; paper, 34 francs.

This is an extract (pages 1169 to 1225) from the Annual Tables, as indicated in the title. The first part consists of ten chapters on colloids and the second part consists of four chapters on adsorption.

It is very interesting to see that colloid chemistry is slowly emerging from the qualitative age. While it cannot be said that we have fully arrived at the quantitative age, this compilation at least shows that we are on the way. Reproducible quantitative data in colloid chemistry are very difficult to get, and of course if data are not reproducible they are of no particular value. The colloid chemists, at least many of them, now realize this difficulty and better technic is developing.

While the data here given are interesting, particularly in the way of showing what has been done, a careful reading of the original article would be necessary in most cases in order to understand the precise conditions under which the data were secured. Naturally all these conditions cannot be given in the Annual Tables, and occasionally they are not given in sufficient detail even in the original article.

Although there is a difference of opinion among colloid chemists as to the value of such tables, the reviewer feels they are worth while, though their limitations must be kept in mind. Colloid chemistry is not yet an exact science.—J. H. MATHEWS

Méthodes et Procédés Métallurgiques. BY M. RÉGNAULD. 342 pages. Gauthier-Villars et Cie., Paris, 1929. Price, 60 francs.

The title of this book is somewhat misleading as, apart from a dozen pages devoted to the minerals from which half a dozen other metals are extracted, it deals entirely with iron and steel. The author, who is chief engineer of naval artillery, planned to set forth methodically the principal facts of (French) iron- and steel-making practice, and in this he has been reasonably successful; the book is an assembly of general information for the interested outsider, but not a discussion of principles or even of details of practice for the chemist or metallurgist.

The reader can probably best judge its usefulness to him from the following list of main headings, with the number of pages allotted to each topic: refractories (17); minerals of the principal metals and their treatment (19); iron alloys (4); fuels and gas producers (14); combustion (14); blast furnace (22); converters (5); electric furnaces (10); open-hearth and other furnaces (32); pig iron (23); steel making (28); costs (11); molds and ingots (40); forging and rolling (31); heat treatment (36). There is a bibliography of twelve entries, the smallness of this number perhaps being accounted for by the author's statement that "metallurgy is a science of which but a small part can be learned from books."—JOHN JOHNSTON

La Gomme de Balata. Un Volume de l'Encyclopédie du Caoutchouc et des Matières Plastiques. BY A. D. LUTTRINGER. 47 pages. A. D. Cillard, Editeur, 49 Rue des Vinaigriers, Paris, 1929.

This book is a brief but reasonably complete compendium of information regarding balata. In 47 pages it covers for balata the botanical origin, habitat, method of collection, packing, shipment, and purification, as well as yields, costs, markets, commercial uses, and methods of chemical analysis. While, as might be expected in a work so condensed, technical detail—particularly that which has to do with structure and special physical behavior—is not greatly elaborated, the information given seems to be accurately derived from reliable sources and is combined in a very readable and logical fashion.

To the rubber technologists of this country, the explanation of the situation with regard to the imminent destruction of many of the important sources of supply and the extreme improbability of development of plantation sources will be of considerable interest. The reasons for variation in the quality of balata obtained from different countries is also clearly explained and should be helpful in judging future possibilities.

This little book serves a useful purpose and would be worth the reading of anyone interested in the subject.—R. P. DINSMORE

Textilchemische Erfindungen. BY ADOLF LEHNE. Lieferung II—1 Juli–1 Dezember, 1927. vii + 70 pages. Lieferung III—1 Januar–30 Juni, 1928. viii + 74 pages. A. Ziemens Verlag, Wittenberg, Germany, 1928. Price, each part, 1.50 marks.

It is a pleasure to welcome the second and third parts of this work, the first part of which appeared a little over a year ago. In Part II there are two patents on finishing, thirty on dyeing processes, seven on printing, fifty-nine on new dyestuffs of various groups, and six on artificial fibers and carbonizing. Part III covers six patents on finishing, thirteen on dyeing methods, six on printing, fifty-five on dyestuffs of various classes, and nine on artificial fibers and carbonizing.

The general style of treatment in these two new issues is the same as in the first part. In the review of that part it was suggested that a more complete discussion of the patents, while still keeping their treatment within the limits of a brief summary, might improve the book. Doctor Lehne makes clear, in a short preface to the third part, the essential value (he puts it on the score of purpose; the word "value" is our estimate) of a brief treatment such as he has thought best. In his words,

> The favorable reception of the first part, in this country and abroad, has shown that, in the circle of the many workers interested in the progress of the textile industry, there has existed a demand for speedy information regarding this progress, step by step, in so far as advances have been made known through the procedures of patents which have been granted. The author has apparently succeeded in so arranging the copious material that an expert can quickly find the patents which are of special interest to him.

These remarks do indicate the great value of his method of treatment—viz., the ability to inform one's self rapidly as to the general bearings of recent patents. The reviewer has already found the first part to be of much value and convenience in determining the existence or non-existence of very recent patent literature upon certain topics, but he cannot help again expressing the wish that the patents of other countries might be included. But, without question, this would make it impossible to keep the work up to date without serious omissions and unavoidable delays; and it is worth while noting that, with the issue of the present third part, we are in touch with the German patent literature up to only six months before that part was received—a record in keeping up to date which it might be hard to equal.

If some expert were to supplement Doctor Lehne's work by a similar digest, as well worked up, of the patent literature of other countries, the textile industry would find itself in possession of an invaluable means of progress. We shall welcome, value, and use the succeeding issues of Doctor Lehne's work.—FREDERICK S. BEATTIE

Halbmikromethoden zur automatischen Verbrennung organischer Substanzen und ebullioskopischen Molekulargewichtsbestimmung. BY EDUARD SUCHARDA AND BOGUSLAW BOBRANSKI. 37 pages, 6 illustrations. Heft 94, Sammlung Vieweg. Friedrich Vieweg & Sohn, A. G., Braunschweig, 1929. Price, 2.75 marks.

Only within the last few years have our analytical control laboratories begun to appreciate the great losses they have sustained through failure to employ microchemical methods of analysis. This neglect has been due largely to the fact that these methods have not been sufficiently exploited, have not yet become standardized, and their proponents have failed to emphasize the time-, labor-, and material-saving qualities of microchemical methods but have stressed ability to analyze very small amounts of material. This last point of view appears to be the one deemed of most importance by the authors of this latest contribution to micro-analytical methods, although the reader is led by implication to read rapidity and economy into the methods described.

In the true micro methods of analysis developed by Donau, Emich, Nicloux, Pregl, and others, the weight of substance used for the analysis does not exceed milligrams; a supersensitive, expensive microbalance is essential, and a certain delicate manipulative dexterity must be acquired before dependable results can be obtained. Emich pointed out that if the quantity of material employed was raised to centigrams our ordinary analytical balances could be employed and we could still keep within the range of economical methods. For these methods he proposed the term "semi-micro methods" (Halbmikromethoden). The authors of this pamphlet have followed Emich's terminology.

Methods are described for the determination, in organic compounds, of carbon and hydrogen by combustion in oxygen, and for the determination of nitrogen by a modified Dumas method. These methods are applicable to both solids and liquids with a probable error of 0.2 per cent. The authors also describe an ingenious apparatus for the determination of molecular weights by the rise-of-boiling-point method.

The directions given are clear, concise, and complete. They constitute a real contribution to micro-analytical methods.—E. M. CHAMOT

Maszanalytische Verfahren und deren Anwendung in Zellstoffabriken; mit Anhang chemische Einwirkung der schwefligen Säure auf organische Stoffe in der Sulfitablauge. BY ERIK OEMAN; translated into German by W. SCHMIDT. 119 pages. Verlag von Zellstoff und Papier; Carl Hofmann, G.m.b.H., Berlin, 1928.

This book consists of five papers, published by the author in Swedish and translated by the publisher into German, on the analysis of solutions used or obtained as waste liquor in the cellulose industry. Part V gives also the results of a special study of the action of sulfurous acid on organic substances in white water.

The first part deals with the determination of sodium hydroxide in sulfide liquor from the sulfate process, the titration of the hydroxide in the presence of carbonate and alkali sulfide. By the application of Nile blue as an indicator the author is able to obtain a fairly accurate approximation of the hydroxide content. The second part, dealing with indicators for the cellulose industry, gives analytical details on the volumetric analysis of the sulfite liquor. It should be remarked that the iodometric titration of sulfide described on page 24 leads to erroneous results. The third part gives a general outline of the hydrogen-ion concentration, especially with regard to the application of indicators in neutralization analyses. Moreover, the titration error is discussed. The fourth paper is analytical again and describes titration methods for black liquor.

For those particularly interested in the analysis of digestion liquors used or obtained after the process in the cellulose industry, the book will give valuable information. The appearance, print, and translation are excellent.—I. M. KOLTHOFF

Proceedings of the Thirty-First Annual Meeting, American Society for Testing Materials. Volume 28. Part I—Committee Reports. New and Revised Tentative Standards. 1184 pp. Part II—Technical Papers. 904 pp. American Society for Testing Materials, Philadelphia. Price, each part, paper, $6.00; cloth, $6.50; half-leather, $8.00.

MARKET REPORT—APRIL, 1929

FIRST-HAND PRICES FOR CHEMICALS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET ON APRIL 15

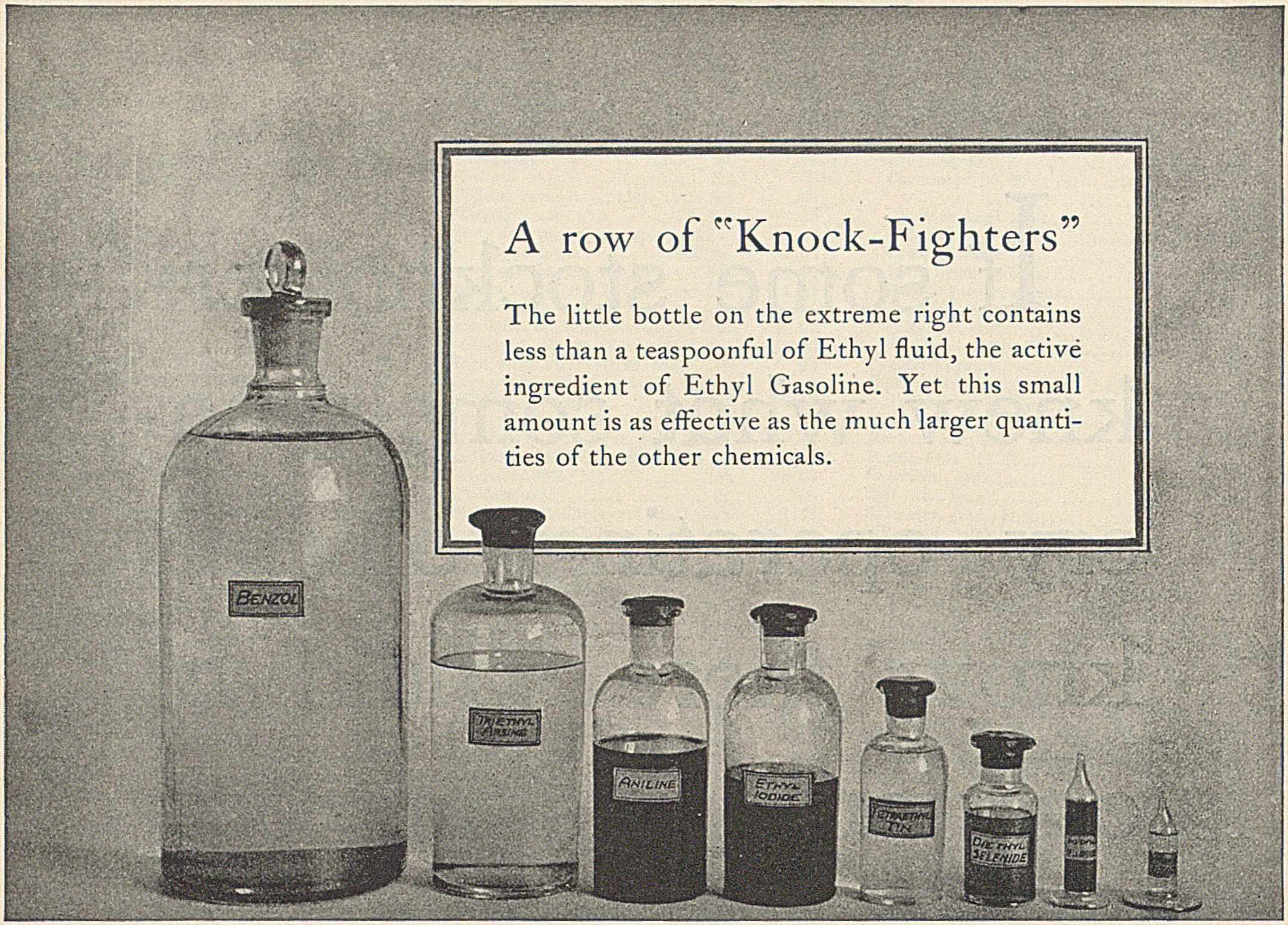
Newer Chemicals

Acetaldehyde, drums, lc-l., wks...lb.	.18½
Acetaldol, 50-gal. drums...lb.	.27
Acetylene tetrachloride, *see* Tetrachloroethane	
Aldol, c/l., wks...lb.	.27
Amyl furoate, 1-lb. tins...lb.	5.00
Butyl carbitol, *see* Diethylene glycol monobutyl ether	
Cellosolve, *see* Ethylene glycol monobutyl ether	
Furoate, tech., 50-gal. drums...lb.	.50
Carbitol, *see* Diethylene glycol monomethyl ether	
Cellosolve, *see* Ethylene glycol monoethyl ether	
Acetate, *see* Ethylene glycol monoethyl ether acetate	
Cellulose acetate, 50-lb. kegs...lb.	1.25
Crotonaldehyde, 50-gal. drums...lb.	.32
Dichloroethylether, 50-gal. drums.lb.	.05
Diethylene glycol, drums...lb.	.10
Monobutyl ether, drums...lb.	.28
Monoethyl ether, drums...lb.	.13
Monomethyl ether, 50-gal. drums...lb.	.17
Diethylene oxide, 50-gal. drums...lb.	
Dioxan, *see* Diethylene oxide	
Diphenyl, c/l...lb.	.40
Ethyl acetoacetate, 50-gal. drums...gal.	.65
Carbonate, 90%, 50-gal. drums...gal.	1.85
Chlorocarbonate, 50-gal. drums...gal.	.35
Ether, absolute, 50-gal. drums...lb.	.50
Furoate, 1-lb. tins...lb.	5.00
Ethylene chlorhydrin, 40-, 50-, 90-gal. drums...lb.	.75
Dichloride, 50-gal. drums...lb.	.05
Glycol, 50-gal. drums...lb.	.25
Monobutyl ether, drums, wks...lb.	.24
Monoethyl ether, drums, wks...lb.	.17
Monoethyl ether acetate, drums, wks...lb.	.20
Monomethyl ether, drums...lb.	.20
Oxide, cyl...lb.	2.00
Furfuramide (tech.), 100-lb. drums.lb.	.30
Furfuryl acetate, 1-lb. tins...lb.	5.00
Alcohol, 100-lb. drums...lb.	.50
Furoic acid (tech.), 100-lb. drums.lb.	.50
Helium, 1-liter bot...liter	25.00
Lead dithiofuroate, 100-lb. drums..lb.	1.00
Magnesium peroxide, 100-lb. cs...lb.	1.25
Methyl acetate, drums...gal.	.95
Cellosolve, *see* Ethylene glycol monomethyl ether	
Furoate, tech., 50-gal. drums...lb.	.50
Paraldehyde, 110–55 gal. drums..lb.	.20½
Phosphorous oxychloride, 175 cyl..lb.	.35
Propyl furoate, 1-lb. tins...lb.	5.00
Strontium peroxide, 100-lb. drums.lb.	1.25
Sulfuryl chloride, 600-lb. drums, crude...lb.	.10
Distilled...lb.	.35
Tetrachloroethane, 50-gal drums...lb.	.09
Trichloroethylene, 50-gal. drums...lb.	.10
Triethanolamine, 50-gal. drums...lb.	.55
Vinyl chloride, 16-lb. cyl...lb.	1.00
Zinc dithiofuroate, 100-lb. drums.lb.	1.00
Perborate, 100-lb. drums...lb.	1.25
Peroxide, 100-lb. drums...lb.	1.25

Chemicals Previously Quoted

Acetanilide, U. S. P., bbls...lb.	.36
Acetic anhydride, 92–95%, cbys...lb.	.29
Acetone, C. P., drums, wks...lb.	.15
Acetophenetidine, bbls...lb.	1.40
Acid, acetic, 28%, c/l. bbls...100 lbs.	4.13
56%, c/l. bbls...100 lbs.	7.35
Glacial, c/l. bbls...100 lbs.	13.68
Acetylsalicylic, bbls...lb.	.85
Anthranilic, 99–100%, drums...lb.	.98
Benzoic, tech., bbls...lb.	.57
Boric, bbls...lb.	.05¾
Butyric, 60%, pure, 5-lb. bot...lb.	.55
Chloroacetic, mono-, bbls., wks..lb.	.21
Di-, cbys...lb.	1.00
Tri-, bbls...lb.	2.50
Chlorosulfonic, drums, wks...lb.	.05
Chromic, pure, 98%, drums...lb.	.21
Cinnamic, 5-lb. cans...lb.	3.25
Citric, U. S. P., kegs, bbls...lb.	.46
Cresylic, pale, drums...gal.	.72
Formic, 85%, cbys., N. Y...lb.	.11
Gallic, U. S. P., bbls...lb.	.74
Glycerophosphoric, 25%, 1-lb. bot...lb.	1.40
H, bbls., wks...lb.	.68
Hydriodic, 10%, U. S. P., 5-lb. bot...lb.	.67
Hydrobromic, 48%, cbys., wks..lb.	.45
Hydrochloric, 20°, tanks, wks...100 lbs.	1.10
Hydrofluoric, 30%, bbls., wks...lb.	.06
60%, bbls., wks...lb.	.13
Hydrofluosilicic, 35%, bbls., wks...lb.	.11
Hypophosphorus, 30%, U. S. P., 5-gal. demis...lb.	.85
Lactic, 22%, dark, bbls...lb.	.04¼
66%, light, bbls., wks...lb.	.26
Mixed, tanks, wks...N unit	.07
S unit	.01
Molybdic, 85%, kegs...lb.	1.25
Naphthionic, tech., bbls...lb	nom.
Nitric, C. P., cbys...lb.	.12
Nitric, 38°, c/l. cbys., wks...100 lbs.	5.00
Oxalic, bbls., wks...lb.	.11
Phosphate, bulk...ton	9.00
Phosphoric, 50%, cbys...lb.	.08
Picramic, bbls...lb.	.65
Picric, bbls., c/l...lb.	.30
Pyrogallic, tech., bbls...lb.	.86
Salicylic, tech., bbls...lb.	.37
Stearic, d. p., bbls., c/l...lb.	.14½
Sulfanilic, 250-lb. bbls...lb.	.15
Sulfuric, 66°, c/l. cbys., wks...100 lbs.	1.35
66°, tanks, wks...ton	15.50
60°, tanks, wks...ton	11.00
Oleum, 20%, tanks, wks...ton	18.50
40%, tanks, wks...ton	42.00
Sulfurous, U. S. P., 6%, cbys...lb.	.05
Tannic, tech., bbls...lb.	.35
Tartaric, U. S. P., cryst., bbls...lb.	.38
Tungstic, kegs...lb.	1.00
Valeric, C. P., 10-lb. bot...lb.	2.50
Alcohol, U. S. P., 190 proof, bbls...gal.	2.69½
Amyl, 10%, Imp. drums...gal.	1.75
Butyl, drums, c/l., wks...lb.	.17¾
Cologne spirit, bbls...gal.	2.67
Denatured, No. 5, comp. denat., c/l. drums...gal.	.48
No. 1, comp. denat., drums.gal.	.49
Isoamyl, drums...gal.	3.50
Isobutyl, ref., drums...lb.	1.00
Isopropyl, ref., drums...gal.	1.00
Propyl, ref., drums...lb.	1.00
Wood, *see* Methanol	
Alpha-naphthol, bbls...lb.	.65
Alpha-naphthylamine, bbls...lb.	.32
Alum, ammonia, lump, bbls., wks...100 lbs.	3.25
Chrome, casks, wks...100 lbs.	5.25
Potash, lump, bbls., wks...100 lbs.	3.00
Soda, bbls., wks...100 lbs.	3.75
Aluminum, metal, N. Y...lb.	.240
Aluminum chloride, anhyd., drums...lb.	.35
Aluminum stearate, 100-lb. bbl...lb.	.23
Aluminum sulfate, comm'l, bags, wks...100 lbs.	1.40
Iron-free, bags, wks...100 lbs.	1.95
Aminoazobenzene, 100-lb. kegs...lb.	1.15
Ammonia, anhydrous, cyl., wks...lb.	.14
Ammonia water, 26°, drums, wks..lb.	.03
Ammonium acetate, kegs...lb.	.34
Bifluoride, bbls...lb.	.21
Bromide, 50-lb. boxes...lb.	.48
Carbonate, tech., casks...lb.	.09
Chloride, gray, bbls...100 lbs.	5.40
Lump, casks...lb.	.11
Iodide, 25-lb. jars...lb.	5.20
Nitrate, tech., cryst., bbls...lb.	.06
Oxalate, kegs...lb.	.35
Persulfate, cases...lb.	.31
Phosphate, dibasic, tech., bbls...lb.	.13
Sulfate, bulk, wks...100 lbs.	2.30
Thiocyanate, tech., kegs...lb.	.40
Amyl acetate, tech., drums...gal.	1.65
Aniline oil, drums...lb.	.15¼
Anthracene, 80–85%, casks, wks..lb.	.60
Anthraquinone, subl., bbls...lb.	.85
Antimony, metal...lb.	.09½
Antimony chloride, anhyd., drums...lb.	.17
Oxide, bbls...lb.	.10
Salt, dom., bbls...lb.	.26
Sulfide, crimson, bbls...lb.	.25
Golden, bbls...lb.	.16
Vermilion, bbls...lb.	.38
Tartrolactate, bbls...lb.	.45
Argols, red powder, bbls...lb.	.08
Arsenic, metal, kegs...lb.	.50
Red, kegs, cases...lb.	.09
White, c/l. kegs...lb.	.03¾
Asbestine, bulk, c/l...ton	15.00
Barium carbonate, bbls., bags, wks...ton	58.00
Chloride, bags, wks...ton	65.00
Dioxide, bbls., wks...lb.	.12
Hydroxide, bbls...lb.	.04¾
Nitrate, casks...lb.	.08¼
Barium sulfocyanate, 400-lb. bbls...lb.	.27
Barytes, floated, 350-lb. bbls., wks...ton	23.00
Benzaldehyde, tech., drums...lb.	.65
F. F. C., cbys...lb.	1.40
U. S. P., cbys...lb.	1.15
Benzene, pure, tanks, mills...gal.	.23
Benzidine base, bbls...lb.	.70
Benzoyl chloride, cbys...lb.	1.00
Benzyl acetate, cbys...lb.	1.30
Alcohol, 5-liter bot...lb.	1.40
Chloride, tech., drums...lb.	.25
Beta-naphthol, bbls...lb.	.24
Beta-naphthylamine, bbls...lb.	.63
Bismuth, metal, cases...lb.	1.70
Bismuth, nitrate, 25-lb. jars...lb.	1.80
Oxychloride, boxes...lb.	3.10
Subnitrate, U. S. P., 25-lb. jars.lb.	2.05
Blanc fixe, dry, bbls...ton	80.00
Bleaching powder, drums, wks...100 lbs.	2.00
Bone ash, kegs...lb.	.06
Bone black, bbls...lb.	.08¼
Borax, bags...lb.	.02½
Bordeaux mixture, bbls...lb.	.10½
British gum, com., c/l...100 lbs.	4.37
Bromine, bot...lb.	.45
Bromobenzene, drums...lb.	.50
Bromoform, 5-lb. bot...lb.	1.65
Butylacetate, 100-gal. drums...gal.	1.38
Cadmium bromide, 50-lb. jars...lb.	1.20
Cadmium, metal, boxes...lb.	.65
Cadmium sulfide, cs...lb.	1.00
Caffeine, U. S. P., 5-lb. cans...lb.	2.80
Calcium acetate, bags...100 lbs.	4.50
Arsenate, bbls...lb.	.07
Carbide, drums...lb.	.05
Chloride, drums, wks...ton	20.00
Cyanide, 100-lb. drums...lb.	.30
Lactate, tech., bbls...lb.	.35

Nitrate, bbls	ton	52.00
Phosphate, monobas., bbls	lb.	.07
Tribas., bbls	lb.	.11
Calcium carbonate, tech., bgs.	100 lbs.	1.00
U. S. P., precip., 175-lb. bbl	lb.	.06½
Camphor, Jap., cases	lb.	.60
Camphor, monobrom, cs	lb.	1.85
Caramel, bbls	gal.	.63
Carbazole, bbls	lb.	.15
Carbon, activated, drums	lb.	.05
Carbon bisulfide, drums	lb.	.05½
Carbon black, cases	lb.	.10
Carbon dioxide, liq., cyl	lb.	.06
Carbon tetrachloride, drums	lb.	.07
Casein, stand. gr., bbls	lb.	.14½
Cellulose acetate, kegs	lb.	1.25
Cerium oxalate, kegs	lb.	.32
Charcoal, willow, powd., bbls	lb.	.06
China clay, imp., bags	100 lbs.	15.00
Chloral hydrate, drums	lb.	.70
Chloramine, U. S. P., 5-lb. bot	lb.	1.75
Chlorine, liq., c/l., cyl	lb.	.04½
Chlorobenzene, mono-, drums	lb.	.09
Chloroform, tech., drums	lb.	.20
Chromium acetate, 20° soln., bbls	lb.	.05½
Coal tar, tanks, bbls., wks	gal.	.07
Cobalt, metal, kegs	lb.	2.50
Cobalt oxide, bbls	lb.	2.10
Cod-liver oil, bbls	bbl.	39.50
Collodion, drums	lb.	.23
Copperas, c/l., bulk	ton	13.00
Copper, metal, elec	100 lbs.	18.50
Copper carbonate, bbls	lb.	.19
Chloride, bbls	lb.	.25
Cyanide, drums	lb.	.55
Oxide, red, bbls	lb.	.18
Sulfate, c/l., bbls	100 lbs.	6.50
Cotton, soluble, bbls	lb.	.40
Cream tartar, bbls	lb.	.27¾
Cyanamide, bulk, N. Y.	Ammon. unit	1.67½
Diaminophenol, kegs	lb.	3.80
Dianisidine, kegs	lb.	3.00
Dibutylphthalate, drums, wks	lb.	.29½
Diethylaniline, drums	lb.	.55
Diethylene glycol, l. c. l. lots, drums	lb.	.11
Carload lots, drums	lb.	.10
Diethyl phthalate, drums	lb.	.24
Diethyl sulfate, tech., drums	lb.	.20
Dimethylaniline, drums	lb.	.30
Dimethylsulfate, drums	lb.	.45
Dinitrobenzene, drums	lb.	.15½
Dinitrochlorobenzene, bbls	lb.	.15
Dinitronaphthalene, bbls	lb.	.35
Dinitrophenol, bbls	lb.	.31
Diphenylamine, bbls	lb.	.45
Diphenylguanidine, bbls	lb.	.36
Epsom salt, tech., bbls., c/l., N. Y.	100 lbs.	1.70
Ether, nitrous, bot	lb.	.90
Ether, U. S. P., drums	lb.	.38
Ethyl acetate, 85%, drums	gal.	.95
Bromide, drums	lb.	.55
Chloride, drums	lb.	.22
Methyl ketone, drums	lb.	.30
Ethylbenzylaniline, 300-lb. drums	lb.	1.05
Ethylene dichloride, tanks	lb.	.05
Chlorohydrin, anhyd., drums	lb.	.75
Glycol, c/l., wks	lb.	.25
Ethyl ether, drums, cars	gal.	1.79
Feldspar, bulk	ton	20.00
Ferric chloride, tech., bbls	lb.	.07
Ferrous chloride, cryst., bbls	lb.	.05
Ferrous sulfide, bbls	100 lbs.	2.50
Fluorspar, 98%. bags	ton	41.00
Formaldehyde, bbls	lb.	.09½
Formaniline, drums	lb.	.38
Fuller's earth, bags, c/l., mines	ton	15.00
Furfural, 500-lb. drums., c/l	lb.	.17½
Glauber's salt, bbls	100 lbs.	.70
Glucose, 70°, bags, dry	100 lbs.	3.14
Glycerol, C. P., drums	lb.	.15
G salt, bbls	lb.	.50
Hexamethylenetetramine, tech., drums	lb.	.62
Hydrogen peroxide, 25 vol., bbls	lb.	.06½
Hydroquinone, kegs	lb.	1.25
Indigo, 20%, paste, bbls	lb.	.15
Iodine, crude, 200-lb. kgs	lb.	4.20
Iodine, resubl., jars	lb.	4.65
Iodoform, bot	lb.	6.00
Iridium, metal	oz.	280.00
Kieselguhr, bags	ton	60.00
Lead, metal	100 lbs.	7.00
Lead acetate, bbls., white	lb.	.13
Arsenate, bbls	lb.	.13
Oxide, litharge, bbls	lb.	.08½
Peroxide, drums	lb.	.25
Red, bbls	lb.	.09½
Sulfate, bbls	lb.	.08¼
White, basic carb., bbls	lb.	.09
Lime, hydrated, bbls	100 lbs.	.85
Lime, live, chemical, bbls., wks.	100 lbs.	1.05
Limestone, ground, bags, wks	ton	4.50
Lithium carbonate, 100-lb. kgs	lb.	1.45
Lithopone, bbls	lb.	.05¾
Magnesite, crude	ton	36.00
Calcined, 500-lb. bbls., wks	ton	48.00
Magnesium, metal sticks, wks	lb.	.85
Magnesium carbonate, bags	lb.	.06
Chloride, drums	ton	36.00
Fluosilicate, cryst., bbls	lb.	.10
Oxide, U. S. P., light, bbls	lb.	.42
Manganese chloride, casks	lb.	.08
Dioxide, 80%, bbls	ton	80.00
Sulfate, casks	lb.	.08
Mercury bichloride, cryst., 25 lbs	lb.	1.58
Mercury, flasks, 75 lbs	flask	124.00
Meta-nitroaniline, bbls	lb.	.72
Meta-phenylenediamine, bbls	lb.	.84
Meta-toluylenediamine, bbls	lb.	.70
Methanol, pure, drums	gal.	.67
Denaturing grade, tanks	gal.	.60
Methyl acetone, drums	gal.	.83
Salicylate, cases	lb.	.42
Methyl chloride, cylinders	lb.	.55
Michler's ketone, bbls	lb.	3.00
Monoethylaniline, drums	lb.	1.05
Naphtha, solvent, tanks	gal.	.35
Naphthalene, flake, bbls	lb.	.05
Nickel, metal	lb.	.35
Nickel salt, single, bbls	lb.	.13
Double, bbls	lb.	.13
Niter cake, bulk	ton	13.00
Nitrobenzene, drums	lb.	.10¼
Oil, castor, No. 1	lb.	.13
China wood, bbls	lb.	.14½
Coconut, Ceylon, tanks	lb.	.08⅜
Cod, N. F., tanks	gal.	.60
Corn, crude, tanks, mills	lb.	.08¾
Cottonseed, crude, tanks	lb.	.08⅞
Lard, edible, bbls	lb.	.15¾
Linseed, bbls	lb.	.102
Menhaden, crude, tanks	gal.	.52
Neat's-foot, pure, bbls	lb.	.15
Oleo, No. 1, bbls	lb.	.11½
Olive oil, denat., bbls	gal.	1.25
Foots, bbls	lb.	.10¼
Palm, Lagos, casks	lb.	.09
Peanut, crude, bbls	lb.	nom.
Perilla, bbls	lb.	.18
Rapeseed, bbls., English	gal.	.88
Red, bbls	lb.	.11⅛
Soy bean, crude, bbls	lb.	.12¼
Sperm, 38°, bbls	gal.	.84
Whale, bbls., natural, winter	gal.	.78
Ortho-aminophenol, kegs	lb.	2.20
Ortho-anisidine, drums	lb.	2.50
Ortho-dichlorobenzene, drums	lb.	.08
Ortho-nitrochlorobenzene, drums	lb.	.32
Ortho-nitrophenol, bbls	lb.	.85
Ortho-nitrotoluene, drums	lb.	.17
Ortho-toluidine, bbls	lb.	.27
Palladium, metal	oz.	46.80
Para-aminophenol, kegs	lb.	1.15
Para-dichlorobenzene	lb.	.17
Para-formaldehyde, cases	lb.	.40
Paraldehyde, tech., drums	lb.	.26
Para-nitroaniline, drums	lb.	.48
Para-nitrochlorobenzene, drums	lb.	.25
Para-nitrophenol, bbls	lb.	.50
Para-nitrosodimethylaniline, bbls.	lb.	.92
Para-nitrotoluene, bbls	lb.	.30
Para-phenylenediamine, bbls	lb.	1.15
Para-toluidine, bbls	lb.	.40
Paris Green, 250-lb. kegs	lb.	.25
Phenol, drums	lb.	.13¼
Phenolphthalein, drums	lb.	1.10
Phenylethyl alcohol, 1-lb. bot	lb.	7.00
Phosphorus, red, cases	lb.	.60
Phosphorus trichloride, cyl	lb.	.35
Phthalic anhydride, bbls	lb.	.18
Platinum, metal	oz.	68.00
Potash, caustic, drums	lb.	.07⅛
Potassium acetate, kegs	lb.	.29
Bicarbonate, casks	lb.	.13
Bichromate, casks	lb.	.09¼
Binoxalate, bbls	lb.	.16
Bromate, cs	lb.	.35
Carbonate, 80–85%, calc., casks	lb.	.05⅜
Chlorate, kegs	lb.	.08½
Chloride	ton	34.55
Cyanide, cases	lb.	.55
Meta-bisulfite, bbls	lb.	.12
Permanganate, drums	lb.	.16
Prussiate, red, casks	lb.	.39
Yellow, casks	lb.	.18½
Titanium oxalate, bbls	lb.	.21
Pyridine, drums	gal.	1.75
Quinine bisulfate, 100 oz	oz.	.40
Sulfate, 100-oz. cans	oz.	.40
Resorcinol, tech., kegs	lb.	1.20
Rochelle salt, bbls., U. S. P	lb.	.23
R salt, bbls	lb.	.45
Saccharin, cans	lb.	1.75
Salt cake, bulk	ton	19.00
Saltpeter, gran., bbls	lb.	.06⅛
Silica, ref., bags	ton	22.00
Silver nitrate, 16-oz. bot	oz.	.40¼
Soda ash, 58%, light, bags, contract, wks	100 lbs.	1.32
Soda, caustic, 76%, solid, drums, contract, wks	100 lbs.	2.90
Sodium acetate, bbls	lb.	.05½
Benzoate, bbls	lb.	.50
Bicarbonate, bbls	100 lbs.	2.25
Bichromate, casks	lb.	.07½
Bisulfite, bbls	lb.	.04
Bromide, bbls	lb.	.42
Carbonate, sal soda, bbls	100 lbs.	1.30
Chlorate, kegs	lb.	.06½
Chloride, bags	ton	12.00
Cyanide, cases	lb.	.18
Fluoride, bbls	lb.	.08¼
Metallic, drums, 12¼-lb. bricks	lb.	.27
Naphthionate, bbls	lb.	.55
Nitrate, crude, bags, N. Y.	100 lbs.	2.22½
Nitrite, bbls	lb.	.08
Perborate, bbls	lb.	.20
Peroxide, cases	lb.	.27
Phosphate, trisodium	lb.	.04
Picramate, kegs	lb.	.69
Prussiate, bbls	lb.	.12
Silicate, drums, tanks, 40°	100 lbs.	1.65
Silicofluoride, bbls	lb.	.05¼
Stannate, drums	lb.	.41½
Sulfate, anhyd., bbls	lb.	.02¼
Sulfide, cryst., bbls	lb.	.02½
Solid, 60%	lb.	.03½
Sulfocyanide, bbls	lb.	.40
Thiosulfate, reg., cryst., bbls	lb.	.02½
Tungstate, kegs	lb.	.70
Strontium carbonate, bbls	lb.	.07¼
Nitrate, bbls	lb.	.09
Strychnine alkaloid, 100 oz., powder	oz.	.46
Sulfate, powder	oz.	.38
Sulfur, bulk, mines, wks	ton	18.00
Sulfur chloride, red, drums	lb.	.05
Yellow, drums	lb.	.03½
Sulfur dioxide, commercial, cyl	lb.	.08
Sulfuryl chloride, drums	lb.	.10
Thiocarbanilid, bbls	lb.	.22
Tin, Amer., stand	lb.	.45
Tin bichloride, 50% sol., bbls	lb.	.14½
Oxide, bbls	lb.	.56
Titanium oxide, bbls., wks	lb.	.40
Toluene, tanks	gal.	.40
Tribromophenol, cases	lb.	1.10
Triphenylguanidine, drums	lb.	.65
Triphenyl phosphate, bbls	lb.	.70
Tungsten	WO_3 unit	14.00
Urea, pure, cases	lb.	.25
Whiting, bags	ton	18.00
Xylene, 5°, drums, mills	gal.	.40
Xylidine, drums	lb.	.38
Zinc, metal, N. Y.	100 lbs.	7.00
Zinc ammonium chloride, bbls	lb.	.05⅛
Chloride, granulated, drums	lb.	.06¼
Oxide, Amer., bbls	lb.	.07⅜
Stearate, bbls	lb.	.25
Zinc dust, bbls., kegs, c/l	lb.	.08½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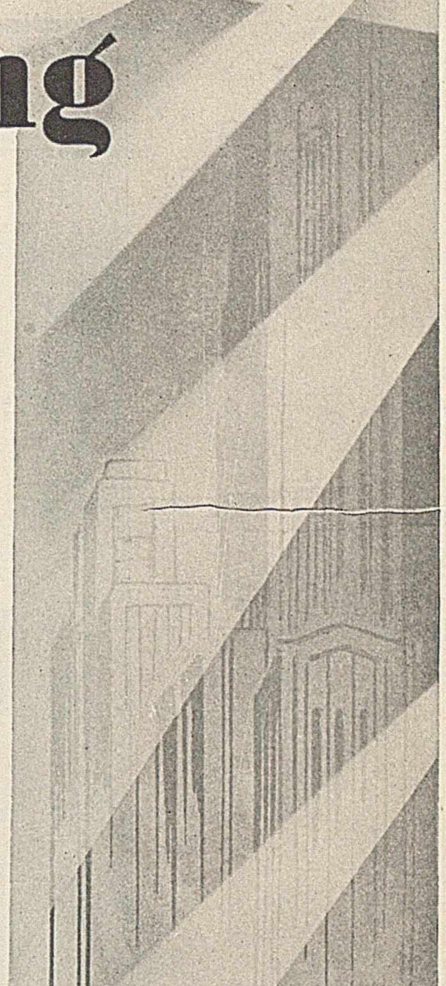
DIETHYL SELENIDE

worth the seeing

A SPECIAL feature of our exhibit will be Baker Spinnerettes for rayon manufacturers. This little instrument through which a solution of cellulose becomes a textile fibre is a marvel of modern mechanical skill. The holes are so minute as to be all but invisible to the unaided eye. Yet every one is perfectly round and smooth and 1-10,000th of an inch is the limit of difference allowed in their size.

You will have the opportunity to examine these holes yourself, through the microscope, and see what specialized modern machines are capable of producing. There will be examples of the various forms of spinnerettes most in use and if you are directly engaged in the textile industry, our people at the Exposition will be happy to go into details with you and explain what we can accomplish for you, how we can aid you in experimenting with precious metal alloys for spinnerettes and how ready we are to consult with you in determining the arrangement, size, and shape of holes best suited to your product.



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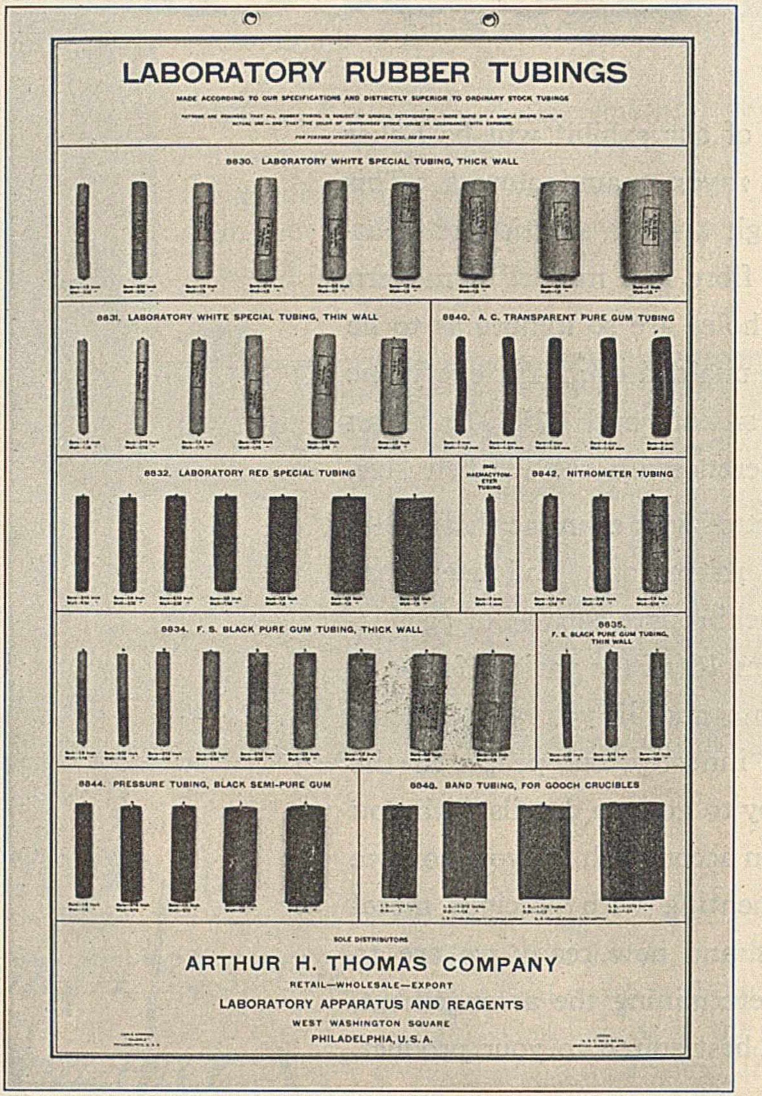

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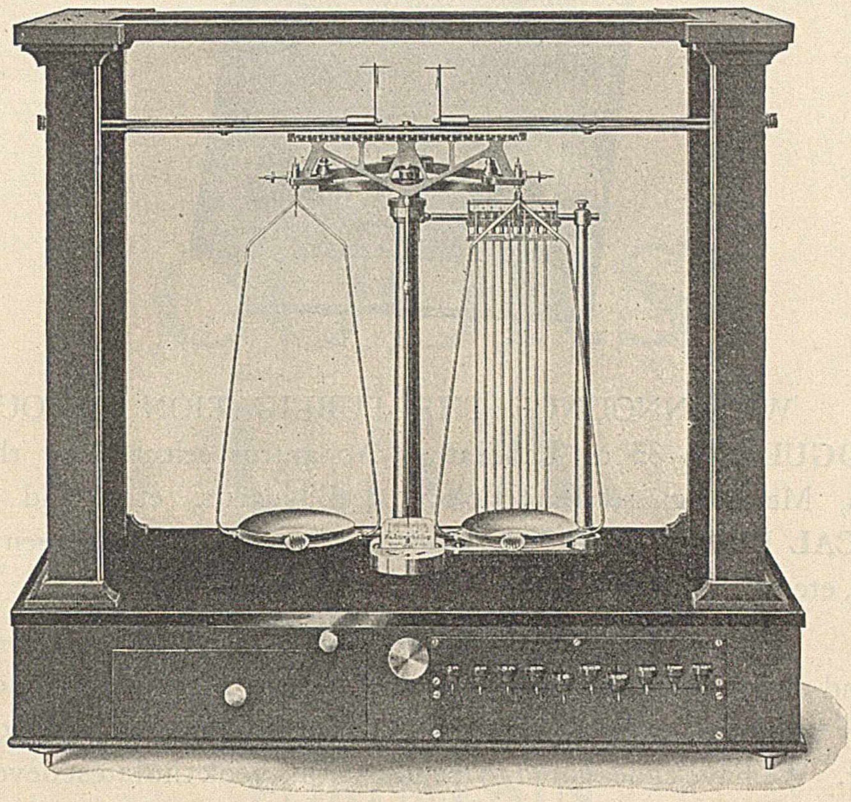

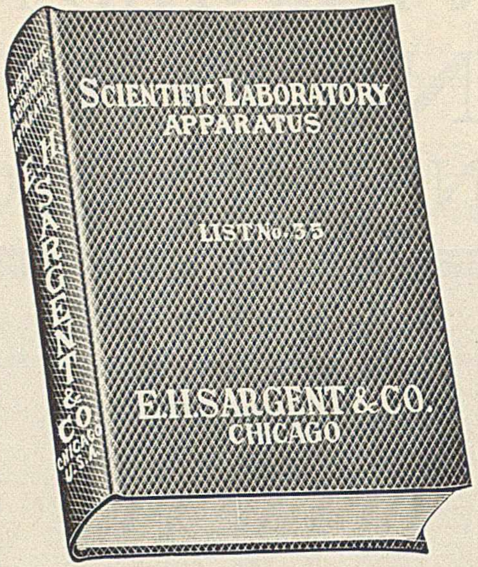
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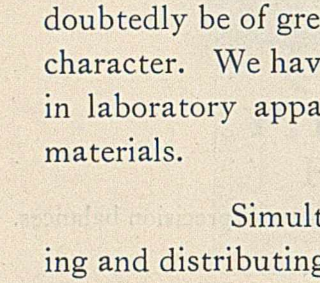

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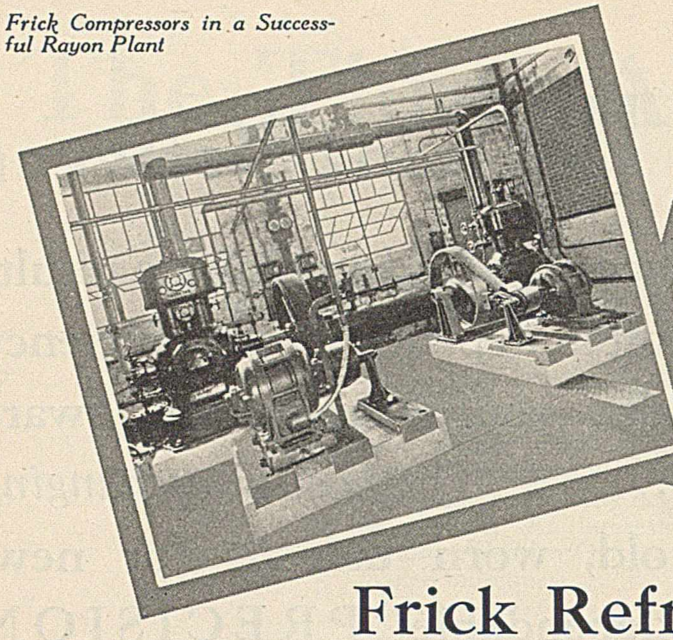

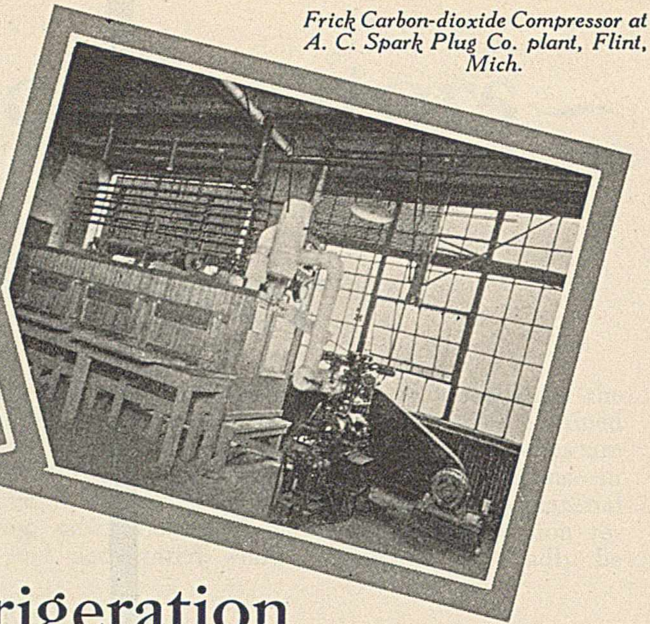

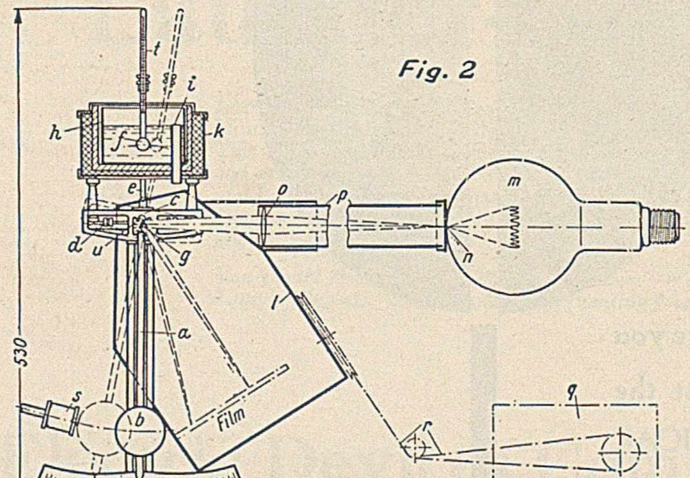
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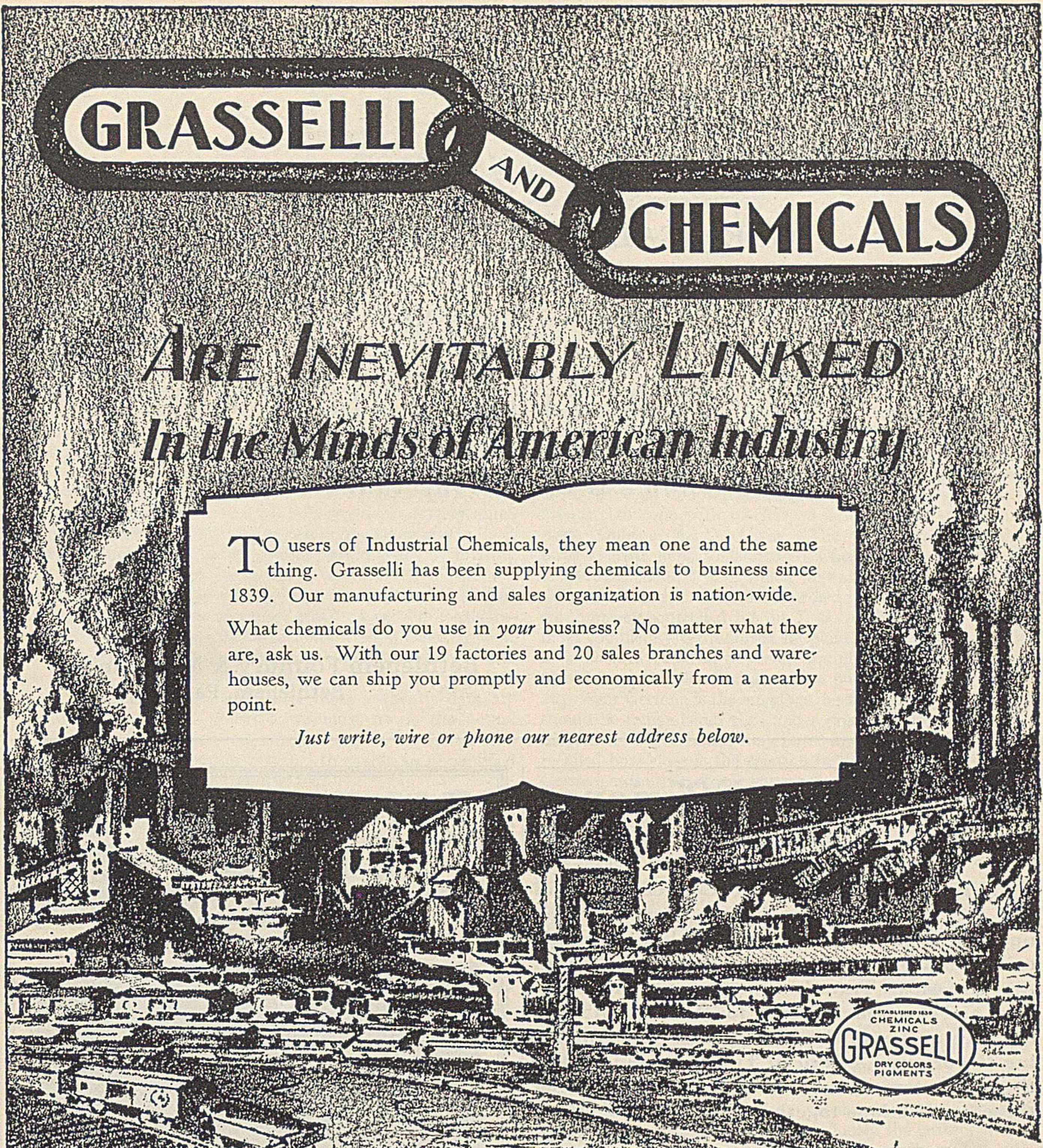
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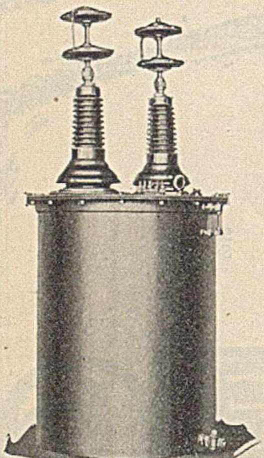

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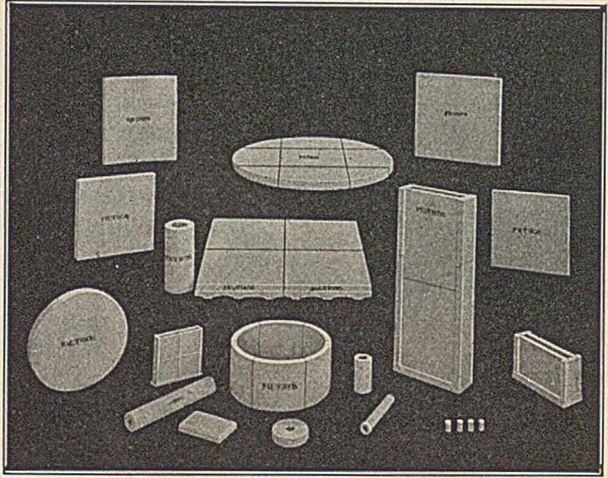

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