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EDITORIALS

Science and Recovery

THE annual meetings of the Chamber of Commerce of the United States bring together a large number of men so important in their various spheres of activity as to lend great weight to their pronouncements.

In a summary of national business affairs published by the Chamber in the *Washington Review* for May 8, 1939, outlining "A Course for Recovery", we find:

> Inventions, scientific discoveries, and new processes have played a constant and vital part in the development of the technology and national progress of the United States throughout its history. As geographic frontiers receded with the increased prosperity and growth of the country, individual enterprise envisioned, developed, and brought to the point of public benefit ever new economic frontiers. New products, new uses, and new industries appeared in never-ending progression.
>
> Great possibilities for enduring expansion in the volume of business and employment lie in the practical application of the results of scientific research. Since 1930 science and invention have far outrun the application of new discoveries and techniques to the use and benefit of the consumer. It is of greatest importance, therefore, that no obstacles be placed in the way of the most intensive utilization of the results of invention and scientific discovery. Ill-advised changes in the patent laws would constitute such obstacles.
>
> It is likewise essential that present deterrents to the investment of capital for the development of new products and processes be quickly removed. Changes in statutory and administrative regulations which are impeding the flow of risk-bearing capital into new enterprise should be immediately effected.

Chemistry Plus

ONE of the most critical periods in life has arrived for many a young man or woman graduate who has devoted several years to preparation for a career in chemistry. Many have already sought and secured places. For others the job is yet to be found.

In seeking employment it will soon be learned that the hard work required to obtain advanced scholastic standing was well spent, for employers are more and more interested in good academic records and many confine their attention to the upper fractions of the class. The applicant for a job will also find that broad training was helpful and that adaptability, which makes it possible for him to qualify for one of several places, rather than specialization, which leads him to think he is best suited to work in a narrower field, is distinctly advantageous. Good habits go without saying, and sound physical health is invaluable.

High standing in chemistry and supporting subjects is taken for granted, but one requires much beyond chemistry. A good personality is the finest asset and those who have not benefited through their own or the efforts of others to develop it are, indeed, to be pitied. There is plenty of room for the individual genius, but he must not be so individual that he fails to cooperate with his group. Fairness, tolerance, honesty, and many other virtues are possessed by those who meet the least difficulty in securing that job.

The May issue of the *Register of Phi Lambda Upsilon* devotes some space to this business of job-getting. Forrest Anderson, who has had much experience in helping young people place themselves, makes ten points which will be helpful guideposts.

1. Secure a correct and selected list of companies who are interested in men of your training.
2. Present a qualification record which puts forth concisely all the facts of your education.
3. Have information at hand about the business and products of the selected companies you are to interview.
4. Present yourself for your personal interview neatly dressed. Be on time.
5. Don't wear out your welcome, but take enough time to present all facts in an endeavor to bring the employer to a definite decision.
6. Summarize clearly all points and agreements before terminating the interview.
7. Make another appointment if the employer wishes you to return at a later date.
8. Exit courteously and avoid flattery.
9. The "follow-up" is important. Send a letter of thanks for the interview. Confirm the important dates and points of the discussion.
10. Persistence in selling yourself to a job is necessary. Marketing man power is not so different from the selling of any other commodity.

Women in Chemistry

WITH only two or three exceptions, the various types of employment available to those practicing chemistry have been filled with credit and distinction by women. While larger numbers are found in some pursuits than in others, this only serves to focus the attention of those who train girls on why this should be true and to raise the query as to what adjustments should be made in the training to overcome any obstacles that may prevent a woman chemist from enjoying the same opportunities offered her brother.

Recently at the Connecticut College in New London, and in cooperation with the Institute of Women's Professional Relations, the question was discussed, "Where Are the Opportunities for Women Chemists?" Nearly all of the participants emphasized the importance of auxiliary skills in opening the door to rewarding opportunities. Secretarial training, library management, advanced filing, abstracting, a knowledge of patent procedure and law were among the skills advocated. Some argued that the preference of industries for men is not because of greater inherent ability but rather because men are more flexible as employees. They can work in many places in an organization which, because of the ordinary setup of industry, have been practically closed to women. One speaker declared that the difficulty existed primarily because of the lack of teamwork among women, plus a lack of aggressiveness necessary in getting above the ordinary laboratory status. The probability of marriage and consequent withdrawal from the service was also believed to be one of the strongest factors in creating prejudice in the industrial field against the advancement of women.

This interesting conference is a splendid introduction to the discussion to be continued before the Division of Chemical Education at the Boston meeting in a Symposium on Training and Opportunities for Women in Chemistry. This is not to introduce the debatable question of women versus men in chemistry, and it is not the intent here or elsewhere to accuse the women of being belligerent in this matter. It is, instead, a serious attempt to examine the whole question in the hope of finding those things which women can do just as well or better perhaps than men chemists. We already know that there are certain fields for which women chemists seem to be particularly well adapted and the most should be made of these. An increasing number of women are being well trained in our colleges and universities, and many of these have chosen science as a career and are vitally concerned in finding a place where service can be rendered wholly on the basis of merit and satisfactory discharge of their duties.

We predict this symposium will attract worthwhile discussion, as well as a large and interested audience.

Disappointing Postponement

AS THIS is written the Senate and the House have in conference a bill which, if it becomes a law, will extend the effective date of the labeling provisions of the new Food, Drug, and Cosmetics Act six months, with another six a possibility for those manufacturers willing to file an affidavit with the Secretary of Agriculture stating that compliance with the law would be unduly burdensome and affirming that the public interest is being adequately served.

We need not remind you how long it took to secure the passage of the act which was intended to enable authorities better to protect the public consumer, nor of pressure which was brought by many groups, usually out of greed and selfishness, to defeat the purposes of the act. When it became a law it surely seemed that the year provided should enable any manufacturer who had the will to do so to be ready upon the effective date of June 25, 1939. Indeed, many such manufacturers are ready, but there are those who say they still have large stocks of goods in hand which would have to be relabeled before they could be shipped, and there are those who claim that the label makers have been so busy that new labels could not be provided. Consequently, the hardship to be worked upon them by conforming with the law is far more important than doing what the law requires for the protection of the consumer. To us it does not make good sense, even though to some it may make cents.

At any rate, those manufacturers and others who take advantage of any extension certainly assume a considerable obligation to the consumer, and must see to it that the public is in effect as well protected where their goods are concerned as if they had seen fit to make themselves ready to comply with the act when scheduled to become law with full force.

Forty Years in Fibers

IF WE are correctly informed, what we now call rayon was first displayed as artificial silk at the Paris Exposition in 1899. The fiber from the laboratory of that day was a considerable advance over that which Count Chardonnet had produced in his effort to do as well as the silk worm. It represented the fruits of long-continued research and financial support that wrecked a company or two before one found out how to make rayon and profits at the same time.

Forty years have passed during which time a number of marked improvements have been made in this chemical fiber. Very little is now produced by even an improved Chardonnet process, and under the name "rayon" there have come fibers which cover a wide range in quality and serviceability resulting from ingenuity, invention, and research poured into an industry that has grown almost beyond belief and now circles the world.

Forty years is a short time for such accomplishments and brings us to the World's Fairs of today where, in place of the fragile fiber of yesteryear, we wonder at the latest fruit of sustained research in organic chemistry—namely, nylon. From a chemical fiber inferior to silk to another superior to it in 40 years is something for which chemistry and those who supported it may be proud. It promises so many advantages to the consumer that one waits with impatience for the availability of the new product on a commercial scale.

CONTINUOUS VULCANIZATION OF BELTING

JOHN M. BIERER AND T. M. KNOWLAND
Boston Woven Hose and Rubber Company, Cambridge, Mass.

The older processes for vulcanizing rubber belting include the use of jaw type presses, the product being intermittently drawn through the press as each succeeding section is vulcanized. The obvious faults of these processes have been reflected in the quality of the products.

As early as 1859 a United States citizen residing in Scotland designed a continuous vulcanizer with a view to eliminating the disadvantages of the jaw press. This machine was a forerunner of other continuous vulcanizing machines, all of them failures in the manufacture of belting and other similar products.

Recently a method has been developed whereby rubber belting of any desired width, length, and thickness can be uniformly stretched, compressed, and vulcanized by means of a continuous process which results in a product of uniform physical and chemical characteristics throughout its length.

FROM the earliest days of the rubber industry it has been realized that a rubber product of uniform quality can be made only by vulcanizing it as a complete unit in one step or by some continuous process. When an article is relatively small, there is little difficulty in vulcanizing it in one step, irrespective of its shape, structure, or composition. On the other hand, when an individual product is very large, and especially when it is very long, it usually has to be vulcanized piecemeal. When a large article, such as a rubber belt, is vulcanized one section after another, mechanical weaknesses and chemical instability of the overcured rubber are introduced. In spite of the fact that the faults of intermittent vulcanization have long been recognized by rubber technologists, the development of machinery and mechanical equipment has, in general, failed to keep pace with developments in compounding. This situation can be attributed to the fact that the development of machines has remained to a great extent in the hands of machinery manufacturers, who, in spite of a willingness to make improvements, have been handicapped by insufficient encouragement and support from the rubber manufacturers.

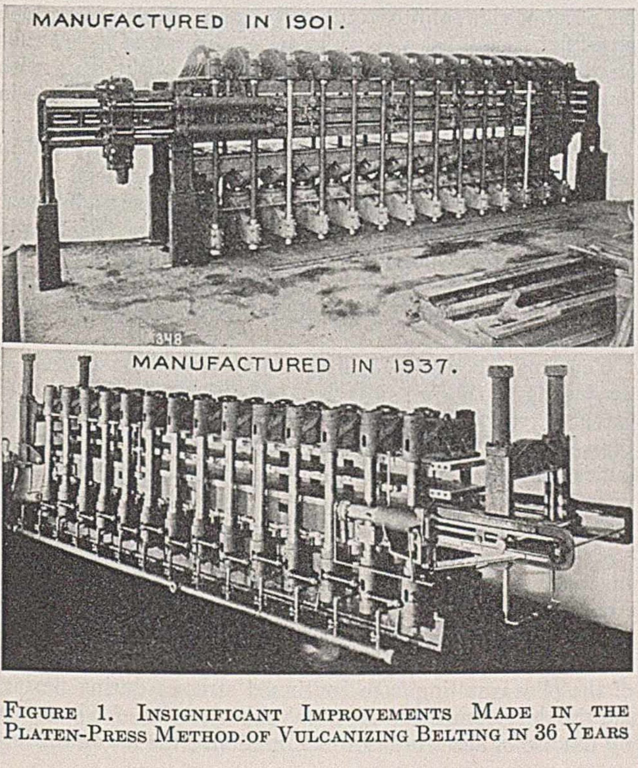


Figure 1. Insignificant Improvements Made in the Platen-Press Method of Vulcanizing Belting in 36 Years

"Continuous vulcanization" means any process whereby a rubber product, no matter how large or how long, is vulcanized progressively and uniformly without interruption at any time or at any point in the article. In this respect there have been two important developments, both made by rubber manufacturers: (1) continuous vulcanization of insulated wire and (2) continuous vulcanization of rubber belting and other mechanical goods.

The first is being used with success industrially, but since it is an adaptation of a very old patent and has been well described in the literature, it will not be discussed here. The second development, the continuous vulcanization of mechanical rubber goods, with particular reference to belting, is the subject of the present paper.

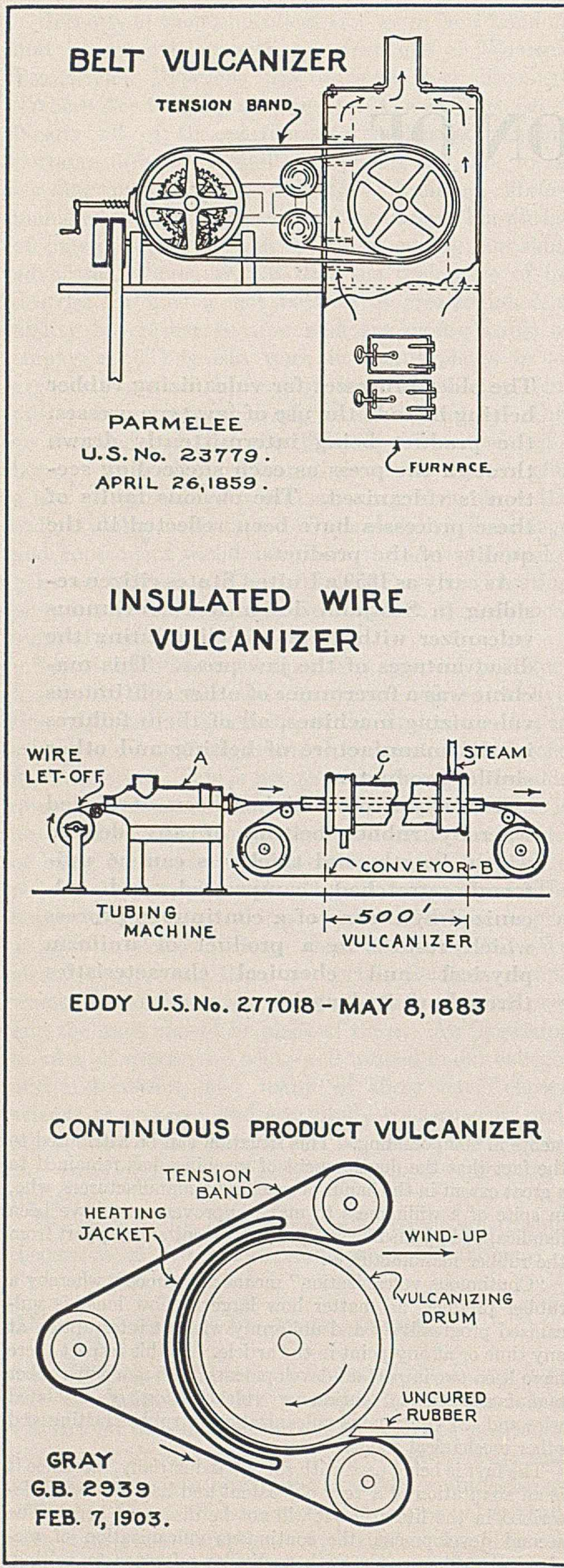


Figure 2. Three Early Attempts at Continuous Vulcanization of Rubber Products

Historical

The improvements which have been made in the platen-press method of vulcanizing belting are only insignificant (Figure 1). These presses, made in 1901 and in 1937 by one of the best known manufacturers of rubber machinery in the world, show no worth-while differences in principles of construction.

A study of the patent literature of different countries brings to light various attempts to vulcanize mechanical rubber products by the continuous method. All these attempts were unsuccessful.

A very early patented machine is shown in Figure 2. In 1859 Parmelee proposed in this patent to vulcanize rubber by passing it over a drum around which was a tension band. Heat was supplied by a fire under the vulcanizing drum. In brief, 80 years ago an inventor realized the harmful effects obtained when a rubber article is not vulcanized continuously.

A machine was patented 56 years ago by Eddy for vulcanizing insulated wire continuously (Figure 2). In effect it is a combination of extruding machine and vulcanizing chamber. In those days there were no rapid accelerators, and curing was relatively slow. Since that time the speed of vulcanization has been increased tremendously and the mechanical faults of the early machine have been overcome.

In 1903 Gray in England obtained a patent for vulcanizing flat rubber articles continuously. His machine (Figure 2) is a notable improvement over the earlier one of Parmelee. However, in spite of the fact that the Gray machine was designed by an executive of a large, progressive rubber factory and was actually constructed, the machine has rested for over 30 years in the department where it was installed, and has never produced any significant quantity of rubber goods.

Belt Making with Platen Presses

Rubber belting is really a laminated structure of rubberized duck, cord, etc., and serious disadvantages have persisted to the present day in its manufacture in platen presses in spite of numerous schemes and devices which have been conceived to overcome these features. From the compounding point of view, antioxidants and organic accelerators which give "flat cures" have aided greatly; also water-cooled ends on the platens have improved conditions. But even with these developments, belts subjected to severe conditions in service frequently break or fail at the press overlap.

Figure 3 shows a belt with a press overlap which failed in oil field pumper service. A survey made in the oil fields, where the service is severe, showed that this has been a frequent cause of failure in belts from every manufacturer. The reason for choosing oil fields as an illustration is that, within a small geographical area, belts of various manufacturers on difficult drives are more readily accessible than in any other field of operation.

The break shown in Figure 3 is to some extent a result of overcuring at the press overlap, but it is to a much greater extent a result of folding of the duck. All belting is compressed about 25 per cent when it is vulcanized, as Figure 4 indicates. Here, outside of the platens, the thicker, still uncompressed section of the belt is clearly seen. When the first section has been vulcanized and this junction of thicker and thinner sections is again vulcanized, the duck at this junction is distorted, badly strained and consequently weakened.

Another frequent way by which transmission belts break down is what is known as "bootlegging"—that is, separation of the plies resulting from continued stresses during flexing. By the development of superior rubber stocks—for instance, by the use of accelerators which minimize the harmful effect of double vulcanization at the end of a platen press—the evil effects of double curing at press ends can be reduced. Nevertheless, tests of belts made by prominent manufacturers show differences of 10 to 40 per cent between the flexing life of the normal parts and the press overlaps of these belts. One manufacturer considers overcuring at the ends of the presses to be so serious that he deliberately undercures the body of his belts in such a way that the press overlaps are properly cured after the double vulcanization. In other words, when this manufacturer sells belting, he sells 29.5 feet of undercured and substandard quality and only 6 inches of good quality.

Press overlaps in conveyor belting are even more serious than in transmission belting. The bad effects on the fabric and on the tendency to "bootleg" are equally serious, but in addition the overcured part of the cover is likely to blister, and resistance to abrasion is lowered by the double cure.

New Developments

Although the earlier machines for continuous vulcanization gave promising results with some types of thin, flat construction, no satisfactory belts have ever been made commercially until recently. The earlier machines did not produce commercially satisfactory belts because they could not be operated under sufficient pressure to give the proper density or compactness of structure to the finished belting, nor were they prestretched. During the last 7 years all these problems have been solved in a machine which is now commercially successful. Figure 5 shows the operation of this machine.

In developing it, no commercial steel could be found of sufficiently high tensile strength to allow the application of pressures high enough to compress the belting to the proper degree. Furthermore, if more strength were to be obtained by increasing the thickness of the band, greater stresses would be set up when the band was bent over the drum and the increased strength would be nullified. Then again, an increase in diameter of the drum would necessitate more tension on the band to compress the belt to a given degree. But it was found that when the belt was first heated and pressure was then applied to compress it to the desired thickness, a steel band of sufficient strength to keep the belt compressed during vulcanization could be secured. The installation and successful operation of a band of this type led to the production of the first sufficiently compact belt ever made on a continuous vulcanizing machine.

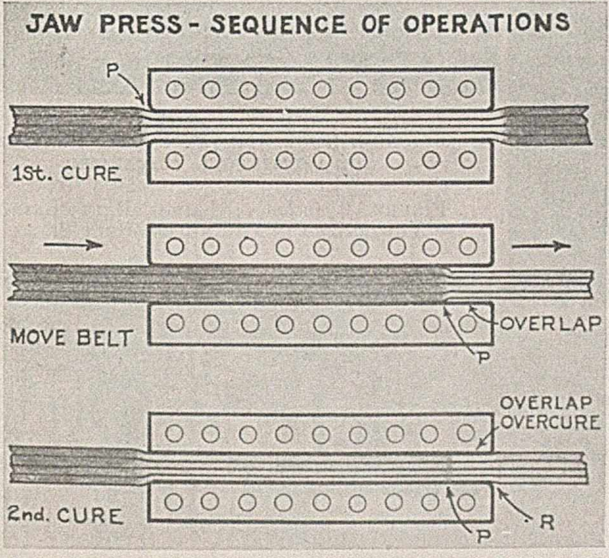


Figure 4

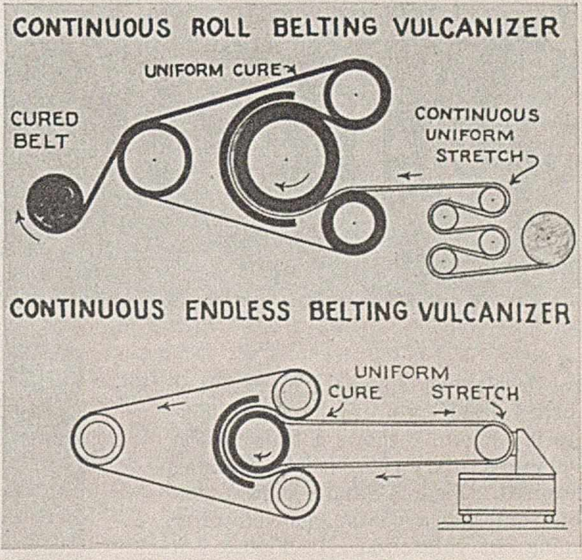


Figure 5

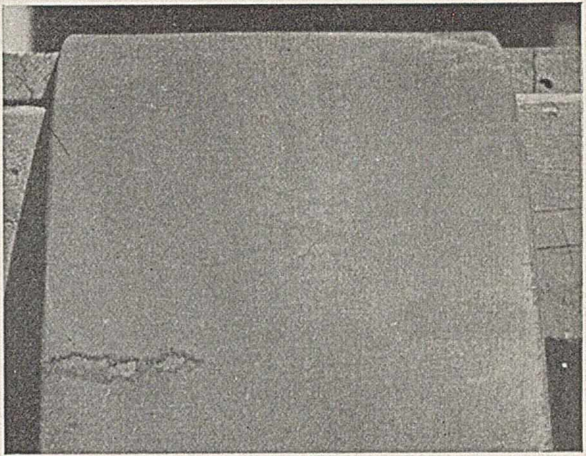
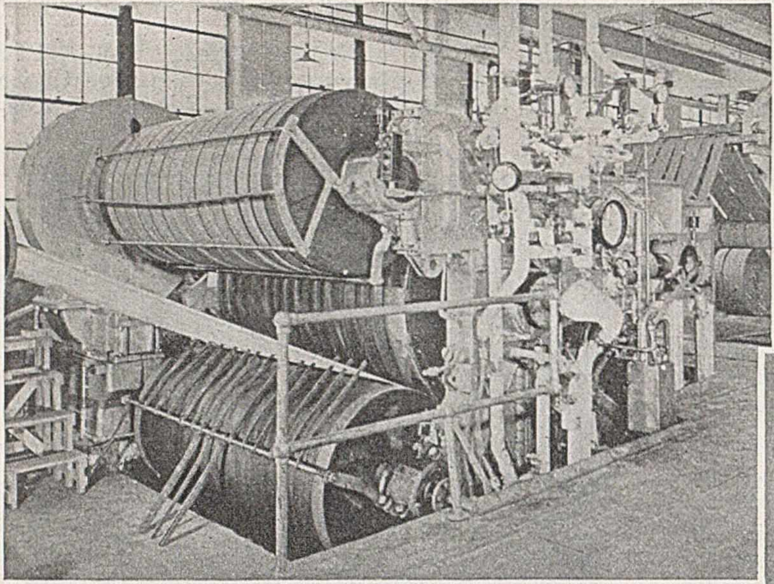


Figure 3. Broken Press Overlap of a Belt Used in an Oil Field

Steel can be rolled in sheets over 10 feet wide, but its quality is wholly unsatisfactory for a vulcanizing tension band. The task was, therefore, to obtain a steel band sufficiently wide and strong to be used for wide belts, particularly conveyor belts. The problem was successfully solved by fabricating a band from narrow, high-tensile strips of steel.

The next problem was to connect the vulcanizing machine directly to a continuous stretching device, whereby the stretch of the belt could be maintained at a predetermined percentage and could also be changed at will by a regulating mechanism. This also was a serious mechanical problem but the design of mechanism finally developed has given satisfactory operation ever since. The principle of vulcanizing endless belts is the same as that for roll belting; only the method of stretching is different.

Finally the problem of making square-edge rubber-covered conveyor belts involved many mechanical problems, the details of which are irrelevant to the present discussion.



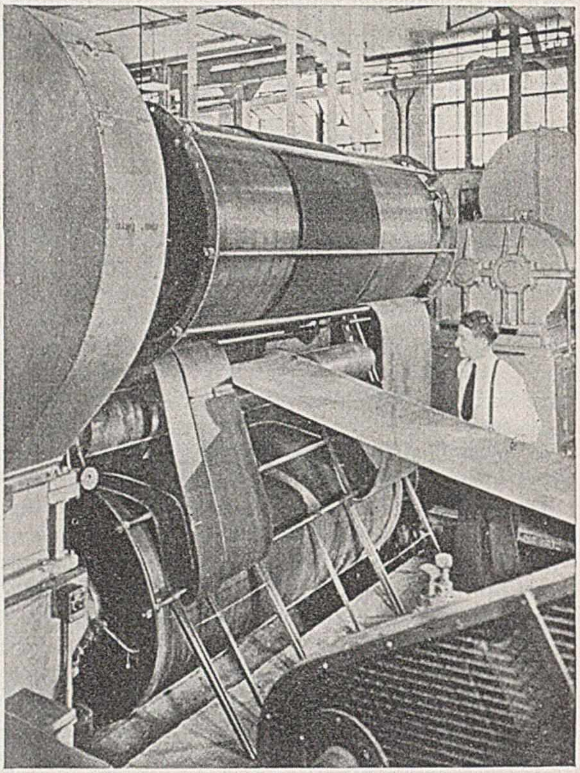


FIGURE 6 (*above*). TRANSMISSION BELT ENTERING A ROTARY VULCANIZER

FIGURE 7 (*right*). CONVEYOR BELT ENTERING A CONTINUOUS VULCANIZER

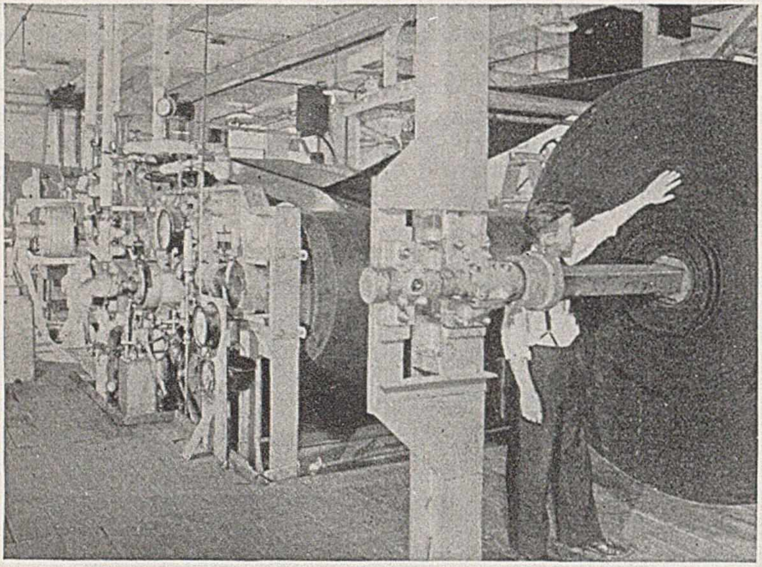
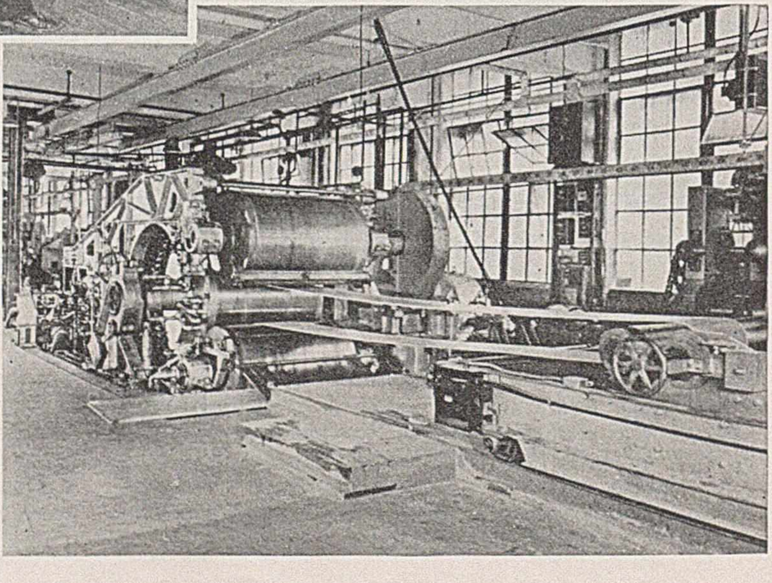


FIGURE 8 (*left*). CONVEYOR BELT LEAVING THE CONTINUOUS VULCANIZER

FIGURE 9 (*below*). LARGE BELT BEING VULCANIZED IN AN ENDLESS-BELT PRESS

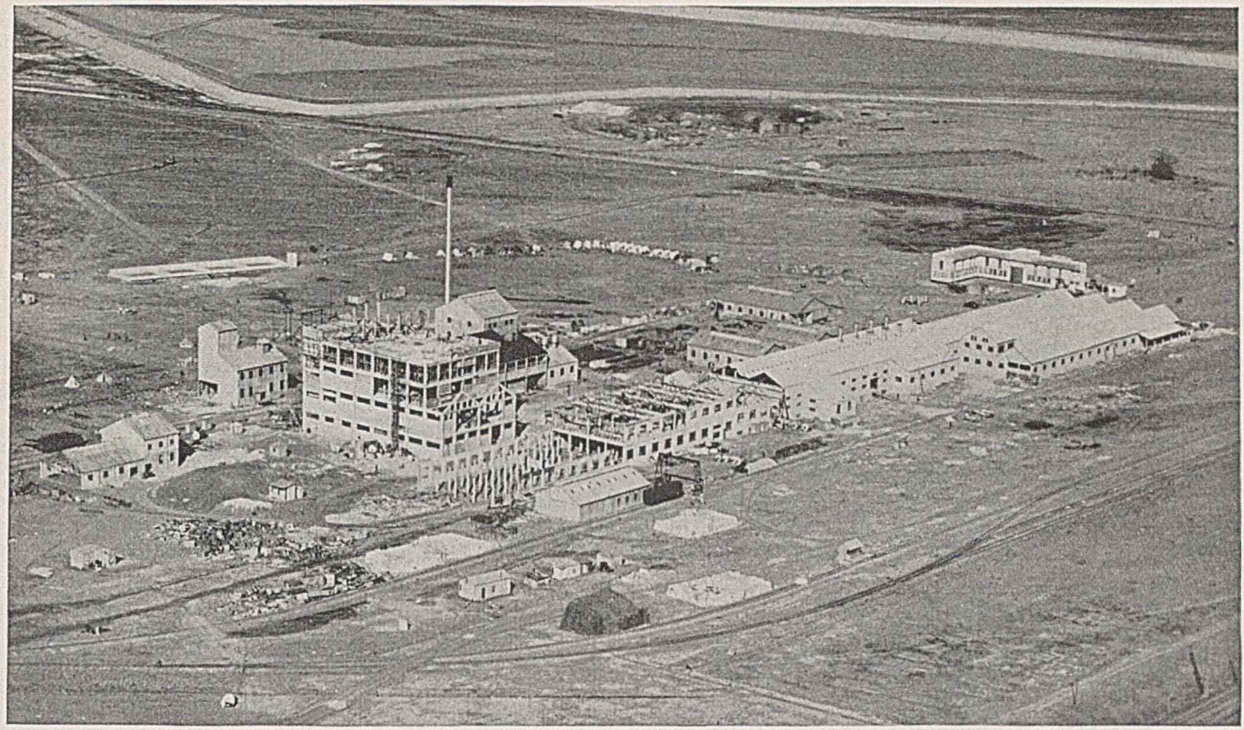


Present developments and the operation of rotary belt vulcanizers are indicated by Figures 6 to 9. Figure 6 shows a transmission belt going into a rotary vulcanizer and coming out vulcanized. Figures 7 and 8 show a conveyor belt entering a continuous vulcanizer and coming out vulcanized. In Figure 9 a large endless belt is being vulcanized in an endless-belt press.

The largest endless belt which has been manufactured by the new method is 52 inches wide and 248 feet long. It is believed that this is the largest truly endless conveyor belt which has ever been made. Many larger conveyor belts have been made endless on the job by a step-splice, but this reduces the strength and the quality of the belts.

The new type of machine for the continuous vulcanization of belting saves steam and hydraulic power. It eliminates the human factor and makes the vulcanization of belts one of the more pleasant and less difficult operations in a mechanical rubber goods plant. The operation of a platen press is hard work and in hot weather is objectionable; in fact, it is one of the most difficult jobs in a rubber factory.

PRESENTED at the 97th Meeting of the American Chemical Society, Baltimore Md.



Aerial View of the South African Pulp and Paper Industries' Factory at Geduld While It Was under Construction

Gas Chlorination in Cellulose Manufacture

UMBERTO POMILIO

South African Pulp and Paper Industries, Ltd.,
P. O. Geduld Station, Transvaal, South Africa

DURING the past ten years a great deal has been published concerning the manufacture of cellulose by chlorination, and in view of misstatements in the technical press (*12*) with regard to the nature, scope, results, and merits of the process, it seems desirable to supply further information.

Gas Chlorination Process

The complete cycle consists of (*a*) predigestion with weak alkali solution at moderate temperature and for a short period, (*b*) exposure of the digested, washed, spongy mass to moist chlorine gas in the cold, (*c*) treatment of the water-washed chlorinated mass with a weak alkali solution and washing, and (*d*) very gentle bleaching with a hypochlorite solution.

Each step is comparatively short; the total time required is not more than 6 to 8 hours, and the first three steps may be completed in 3 to 4 hours.

The only chemicals needed are weak caustic soda solution for steps *a* and *c*, gaseous moist chlorine for step *b*, and hypochlorite for step *d*. The ratio of soda to chlorine may vary and may be made the same as that obtained by electrolytic decomposition of brine; therefore it is necessary only to add a cell room to the pulp plant and use the chemicals as obtained from the cells.

In contrast with other industrial cellulose methods, the gas chlorination, or Pomilio, process is continuous throughout its complete cycle. It does not digest under pressure and generally does away with the recovery of black liquor. Water pollution is generally not to be feared.

Grasses, straw, agricultural by-products in general, textile residues, and wood (whether resinous, free of resin, hard, or soft) all give satisfactory yields of cellulose with the soda-chlorine treatment.

The final products may vary within wide limits; that is, the cellulose may be bleached or unbleached, of high purity for chemical uses, or semichemical pulp to be substituted for groundwood.

Reference to the classical works of Cross and Bevan and to the more recent work of Dorée (*2*) will indicate the superiority of this soda-chlorine process as an extraction method. Apart from a sound theoretical basis, the process has proved practical on a large scale. Wenzl, who was one of the first cellulose specialists to grasp the importance of the

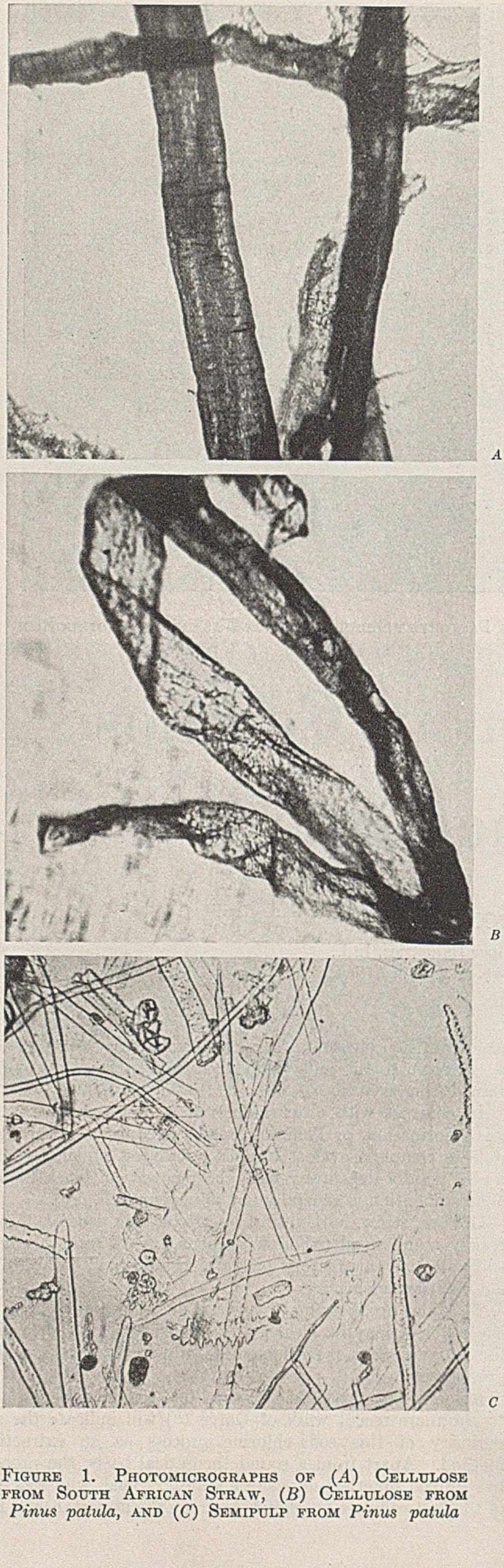


FIGURE 1. PHOTOMICROGRAPHS OF (*A*) CELLULOSE FROM SOUTH AFRICAN STRAW, (*B*) CELLULOSE FROM *Pinus patula*, AND (*C*) SEMIPULP FROM *Pinus patula*

chlorination process, included in his book (*11*) a survey of the gas chlorination process, and gave figures on chemicals consumed, yields, and efficiency (in each case wheat straw of the same origin was used):

Process	Hypochlorite %	Chlorine Gas %	Chlorine Water %	Alkali %
Sodium hydroxide:				
Used on dry straw	7.6	7.0	12.5	22.4
Consumed on dry straw	6.9	6.8	6.9	11.0
Used on cellulose obtained	16.87	14.56	44.6	54.6
Consumed on cellulose obtained	15.35	13.95	24.6	26.8
Chlorine:				
Consumed on straw	18.4	24.8	15.0	..
Consumed on cellulose	40.8	51.7	53.5	3.0
Yields, air-dry	45.0	48.0	28.0	41.0
Efficiency	65.4	76.5	43.3	58.3

Contrary to misstatements that have appeared in the public press, the raw material for the gas chlorination process is salt, and not soda and chlorine.

The principle of the process is elemental chlorine as a chlorinating (delignifying) agent, and not a bleaching (oxidizing) agent. If a bleach liquor is used with the same amount of chlorine as in the gas chlorination process, the yield is lowered and the quality is spoiled. Fifteen years of experience have shown that high pressure is objectionable. The long time required for cooking and the longer period for bleaching involves a considerably higher cost for installation and operation in the case referred to by Wingfield *et al.* (*12*).

In the digestion, which is carried out with soda concentrations and temperatures relatively low and of short duration, cellulose material is not attacked. A soda solution containing between 1 and 3 per cent by volume of sodium hydroxide has no effect on cellulose below 100° C. in the case of grasses, straws, etc., and between 125° and 135° C. in the case of woods, especially if digestion is only partial—that is, if a large amount of noncelluloses is left to act as a shield.

In the next step the material is submitted to a continuous stream of chlorine gas (continuous process), and therefore the concentration of this reagent is constant. No other pulping process has solved this important point, which accounts for a substantial saving of time.

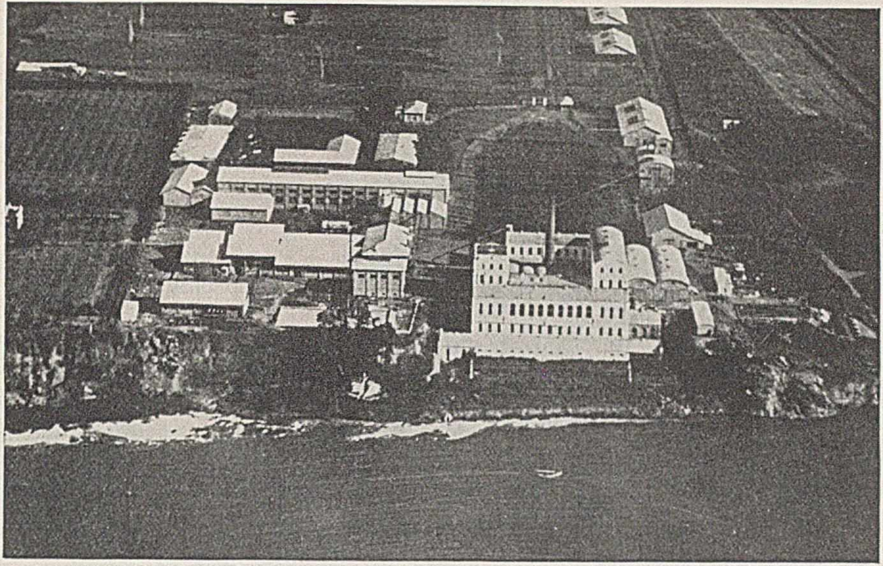
The next favorable condition is that, during the chlorination by gas, a definite pH is created in the mass. The higher the lignin content, the greater the quantity and proportion of hydrochloric acid formed and the higher the pH of the mass. This acidity establishes an ideal condition for the prevention of hypochlorous acid formation—that is, of oxidation, which is a very rapid reaction. The combined action of hydrochloric acid and heat tends to hydrolyze cellulose, but this is a much slower reaction, and only strong acidity and temperatures never reached during chlorination accelerate it.

The alkali wash is a rapid operation which requires only a few minutes. Therefore the process is characterized by rapidity, efficiency, and safety. Since it is a multistage process, the quality of production may be raised before the final stage is reached; this is of paramount importance (*7*).

That delignification and defibering of cellulosic fibers by the chlorination process are complete is shown by photomicrographs (Figure 1) of straw cellulose, *A*, and of pine wood, *B*. Yet the yields are high, and generally over 95 per cent of the theoretical cellulose content of the raw material is extracted in a large-scale operation. However, semichemical pulps, with higher yields and lower costs, may be obtained if desired. Figure 1*C* is a photomicrograph of semipulp obtained from the same South African *Pinus patula* from which pure cellulose (Figure 1*B*) was obtained.

Chlorination Process in the United States

The possibility of producing cheap semipulps, from both woods and straws or grasses, at a price comparable in some cases to that of mechanical pulp and of a quality suitable for



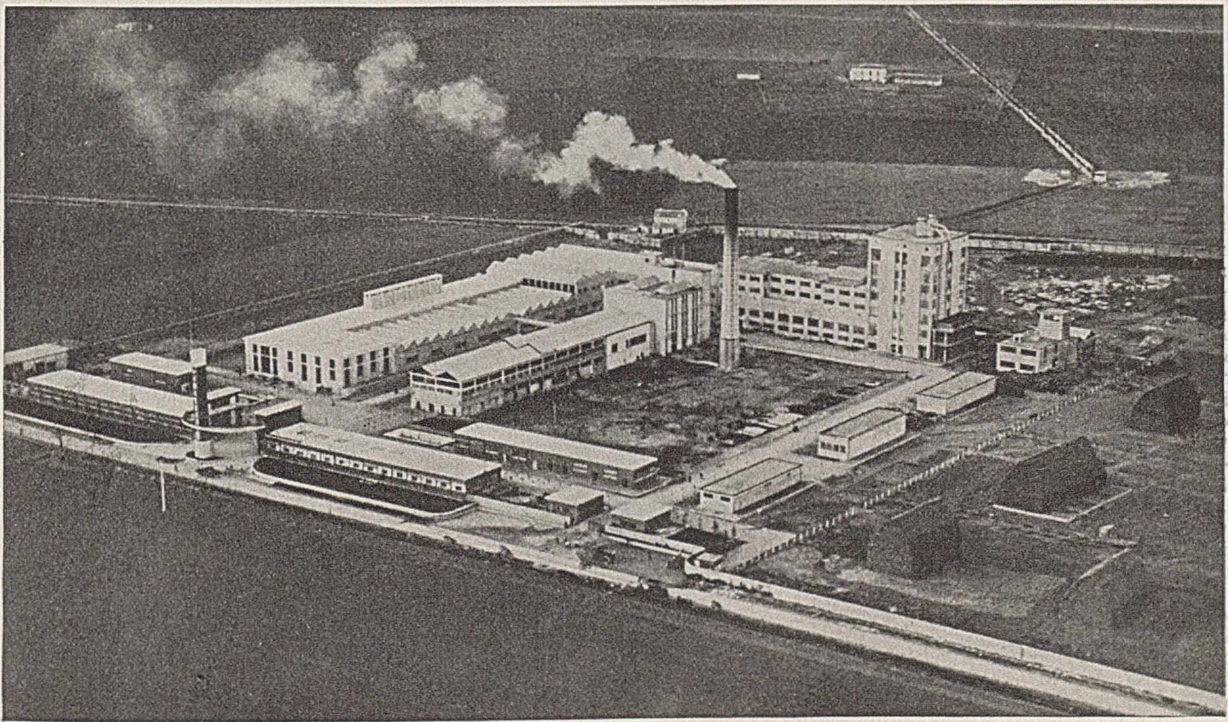
The Plant of Celulosa Argentina, at Rosario, Argentina

newsprint paper, should attract attention. There has recently been considerable agitation in the United States for making newsprint from cereal straws as was done in Italy more than ten years ago (*1*).

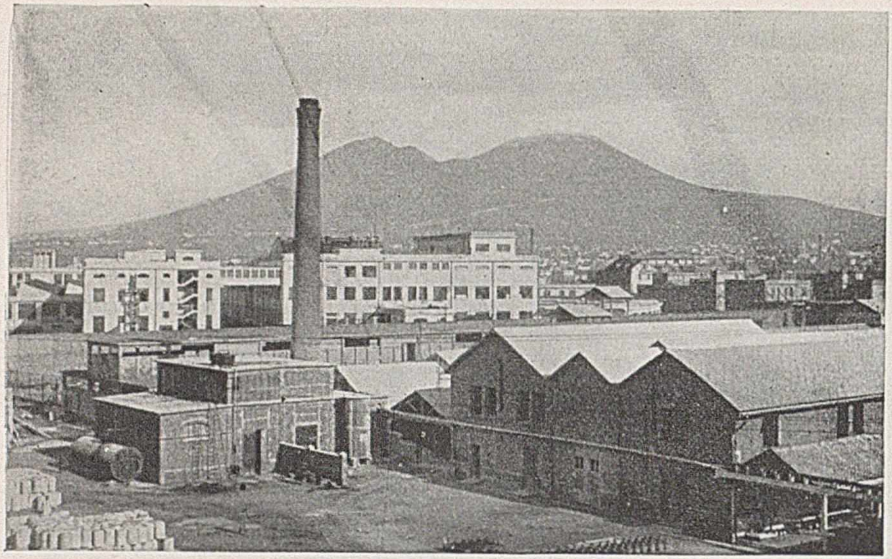
The problem of cellulose production by chlorination has probably attracted less attention in the United States than in any other country, despite the fact that it would be very suitable for American requirements. The process is rapid, and the total time required is about half that necessary for sulfite or sulfate cooking. A total of 4 hours (2 for digestion, 1.5 for chlorination, and 0.5 for alkali wash) is sufficient, compared with an average of 8 hours or more for sulfite or sulfate cooking, from the introduction of chips into the digester to their discharge.

Since the gas chlorination process is continuous throughout, utilization of machinery is 100 per cent as against an average of 50 to 60 per cent for the batch process, so that the cost of the plant per ton output is reduced to about one fourth. In addition, the chlorination process does away with equipment for the recovery of waste liquor.

The process applies industrially to any raw material; grass, cereal straws, hemp stalk, flax straw, rice straw, esparto, bagasse, alfa grass, poplar wood, and pine wood are materials from which cellulose has been or is to be produced on a large scale. It is therefore possible to select any fibrous raw material; in addition, salt and power, both steam and electrical, are needed. The difficulties in straw collection were covered in a recent lecture (*10*).



The Incedit Plant at Foggia, Italy



THE FACTORY OF CELLULOSA CLORO-SODA AT NAPLES

The combined use of wood and straw is possible in a gas chlorination plant, since the digestion black liquors from wood treatment are directly used for cooking straw. Woods, especially if resinous and hard, necessitate a higher soda concentration and temperature during preliminary digestion and result in a higher soda residue in the black liquor. It has been proved (*3*, *5*) that residual black liquors, such as those from soda-digested pine, are an excellent cooking liquor for cereal straws. This combined use of pine wood and straw suggest the feasibility of the process for the southern part of the United States.

Treatment of Wastes

Waste waters from a soda-chlorine pulp plant may be the following:

Black liquor (spent lye after digestion) is the result of a mild digestion carried out with soda at a concentration less than that required to combine with the materials treated. The resulting black liquor is nearly neutral (2 to 3 grams of free sodium hydroxide per liter) and contains about 15 to 20 per cent of the original weight of organic material dissolved or in colloidal suspension. It absorbs oxygen proportionally more, generally, than ordinary sewage waters.

Wash waters from digested materials are similar to but much more dilute than the black liquor.

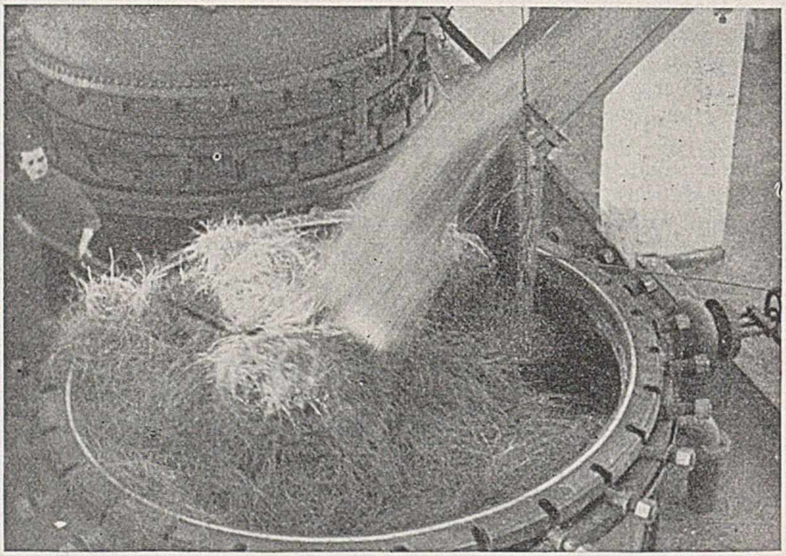
Acid wash waters after chlorination contain free hydrochloric acid (generally less than 1 gram per liter) and traces of dissolved chlorolignin (one of the chlorolignins formed appears to be slightly water soluble).

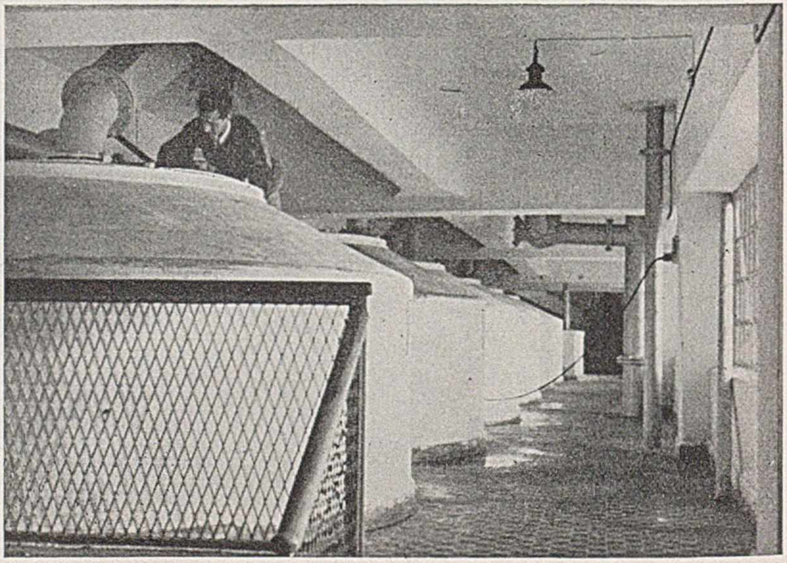
Spent lye after alkalization may be considered as a black liquor, but it is more nearly neutral and contains the alkaline derivatives of the chlorolignins, which are oxygen absorbing.

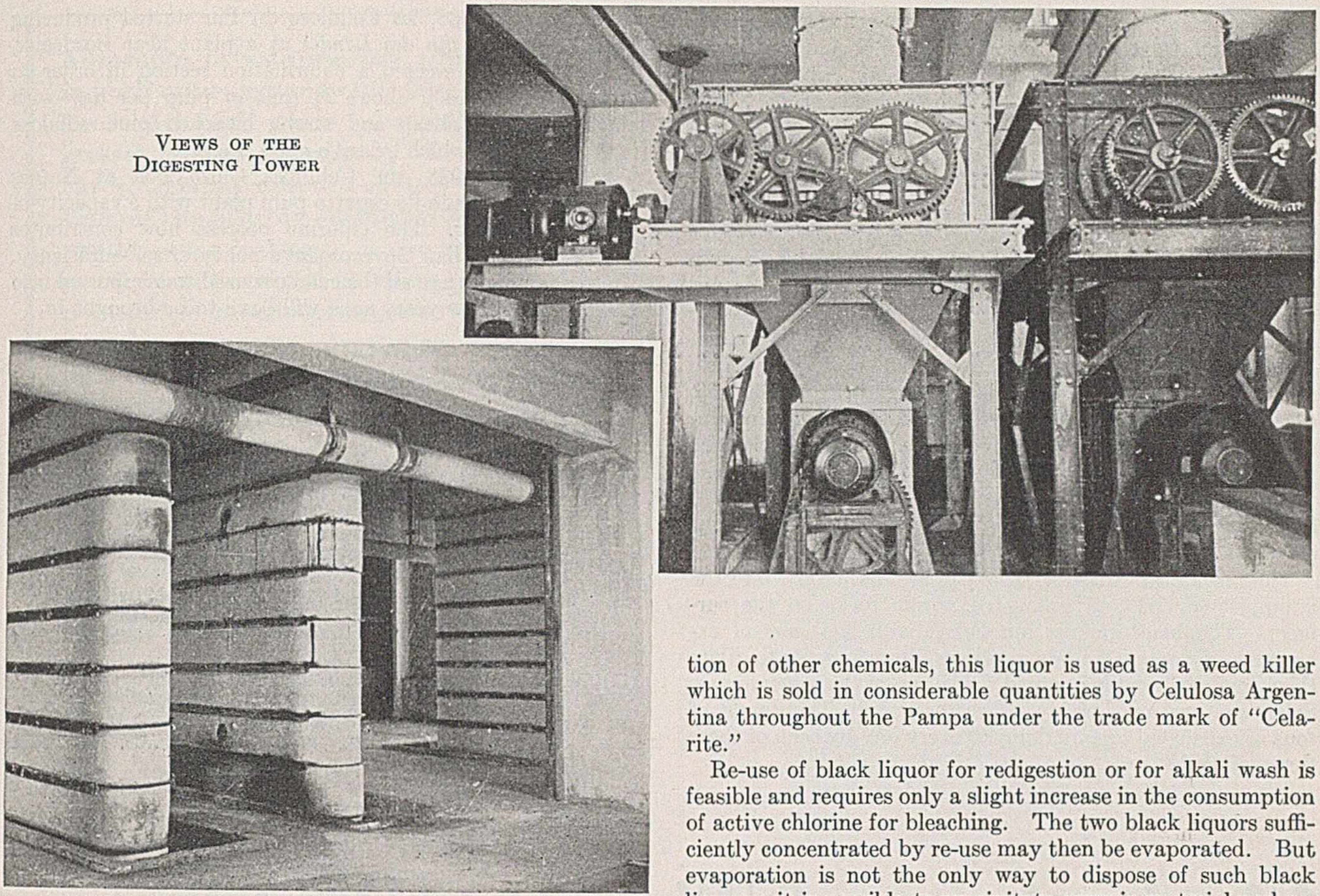
The waste from the washing of pulp after alkalization is a much more dilute solution than the spent lye.

The wash waters after bleaching may contain, in addition to traces of calcium chloride, the last residues of active chlorine, which will be immediately destroyed by the oxygen-absorbing capacity of some of the other waters. The acidity of the wash water after chlorination is obviously neutralized by the spent lye after digestion.

VIEWS IN THE NAPLES PLANT: (*top*) LOADING ESPARTO GRASS INTO THE DIGESTING TOWERS; (*bottom*) SILOS







VIEWS OF THE DIGESTING TOWER

The admixture of the six effluents is practically neutral, nonfermentable, considerably diluted by wash waters, but oxygen absorbing at an extremely slow rate. In contrast to sulfide liquors, the effluent from the chlorination pulp mill does not contain sulfur compounds; its principal mineral constituent is sodium chloride, regenerated from soda and chlorine compounds, but sodium chloride is present to a less extent than in sewage waters. The organic materials are the encrustants from which the cellulose was freed, but because of the high yield no degradation products of cellulose complicate or increase the black liquor problem. The combination of the six effluents is thoroughly mixed and discharged as sewage. The plant at Rosario, Argentina, now discharges into the Paraná River, the Santiago, Chile, factory into a small river, and the plant at Foggia, Italy, into marsh lands since no outlet to sea or river is available; the Naples factory has for some years discharged all waste water into the near-by harbor. In no case have difficulties with effluents been experienced. The plant at Springs, South Africa, will discharge black liquors into the gold-mine dumps. Should special conditions arise by which the disposal of the effluents, especially black liquor and spent lye, must be handled otherwise, the problem will become economic rather than technical.

Black liquor may have sodium hydroxide added to it and be re-used for digestion before it is evaporated and burned, and its volume may be thus reduced; or it can be used for the alkali wash. Its small amount of free residual alkali is thus utilized and its concentration of organic materials increased. Both of these treatments have been carried on at Rosario for years, not to decrease the volume of the waste water but to prepare a strong liquor of small volume. After the addition of other chemicals, this liquor is used as a weed killer which is sold in considerable quantities by Celulosa Argentina throughout the Pampa under the trade mark of "Celarite."

Re-use of black liquor for redigestion or for alkali wash is feasible and requires only a slight increase in the consumption of active chlorine for bleaching. The two black liquors sufficiently concentrated by re-use may then be evaporated. But evaporation is not the only way to dispose of such black liquors; it is possible to precipitate organic material and recover salt.

The gas chlorination process is being developed in countries where no previous pulp industry existed—for example, Argentina, Chile, Uruguay, Brazil, the Transvaal, the Philippines, Italy, etc. (*4*).

Recent Developments

In 1937 a short account of initial operations in the Foggia plant was presented (*9*). After two years the results have proved so satisfactory that production of wheat straw pulp by the chlorination process has more than doubled. Another large wheat straw pulp factory is now being erected by Cellulosa d'Italia at Chieti, Italy, with a capacity of 60 tons per day of bleached high-grade straw pulp, and operations are expected to commence in October, 1939. During 1939 the plants at Montevideo, Uruguay, erected by Fabrica Nacional de Papel, with a capacity of 18 tons per day of bleached straw pulp and at Central Bais, Philippine Islands, built by Compania General de Tabacos, with a capacity of 12 tons per day of rayon from bagasse, will start production. Another plant which utilizes esparto and broom is being erected at Castelraimondo, near the famous Fabriano paper mills in central Italy.

Celulosa Argentina began at Rosario with an output of 12 tons of pulp per day in 1930, increased it to 40 tons by 1937, and in August, 1938, successfully started a second wheat straw pulp plant with a production of 40 tons per day. A gas chlorination unit of latest design was used; it is continuous throughout and includes digestion. Celulosa Argentina began in 1929 with a capital of 1,500,000 pesos and one paper machine, and now has a capital of 18,000,000 pesos and twelve paper machines in three factories. The production of chemicals connected with brine electrolysis has been so developed that at present about 50 per cent of the profits come from the sale of such chemicals as caustic soda, hydrochloric acid, sodium hypochlorite, bleaching powder, chlorides, liquid chlorine, and synthetic ammonia, both anhydrous and in solution, made from by-product hydrogen gas. This shows the elasticity of the gas chlorination process; the pulp and paper factory may or may not enter the chemical market and, if it chooses, can do so on a very profitable basis.

The plant of the South African Pulp and Paper Industries, Ltd., at Springs, near Johannesburg, Transvaal, began operations in December, 1938 (*6*, *8*). There are both straw pulp and pine pulp units; both are producing bleached or unbleached chemical pulp as well as semichemical pulp. The caustic soda, in concentration of 3 to 4 per cent of sodium hydroxide, is used to cook pine wood under slight pressure; and the black liquor obtained, containing about 1.5 per cent of sodium hydroxide, is utilized for cooking straw in continuous digestion towers under atmospheric pressure. The plant, located near three large gold mines, will supply the water pumped from their shafts, which sink as low as 6000 feet. (The Johannesburg Rand is on a high plateau about 6000 feet above sea level.)

The black liquors and some waste are discharged into the "dumps" (milled and exhausted aurific rocks on the surface). The black liquors are mixed with the cake of exhausted ore coming from huge Oliver filters in order to dilute them, and the mud is pumped to the top of the mine dumps. Solar evaporation quickly dries the mud. Thousands of tons of exhausted ore are dumped every day by each of these three mines.

In January, 1938, La Cellulose du Pin started producing kraft pulp from *pin des Landes* at a plant near Bordeaux, France, and has erected a chlorination section in order to delignify and bleach about 24 tons of pulp per day with chlorine gas; a cheap and strong bleached pine cellulose is thus obtained which brings a good price.

In October, 1938, the Cellulosa Cloro-Soda at Naples started operations in its esparto pulp plant with a capacity of 24 tons per day. The chlorine process now contributes largely to the Italian Government's policy of self-sufficiency. Up to a few years ago all the cellulose used was imported into Italy, but in a few years none will have to be brought in.

Literature Cited

(1) *Chimie & Industrie*, 18 (Oct., 1927).
(2) Dorée, Charles, "Methods of Cellulose Chemistry", 1933.
(3) Dupont, G., and Fayard, J. de, *Chimie & Industrie*, 31, No. 4 bis, 784–7 (1934); *Bull. soc. chim.*, 28, 175 (1877).
(4) Electrochem. Soc., miscellaneous notes.
(5) Fremy and Urbain, *Bull. soc. chim.*, 37, 409 (1882).
(6) Grove, J. E., *South African Printer & Stationer*, 18, 227 (1938).
(7) Hall, Gösta, "Some Aspects of Modern Pulp Manufacture", Paper Makers Association of Great Britain and Ireland, 1937.
(8) *Paper Trade Rev.*, Technical Convention No., March, 1938.
(9) Pomilio, Umberto, IND. ENG. CHEM., News Ed., 15, 73 (1937).
(10) Pomilio, Umberto, "Use of Chlorine Gas in Industrial Pulp Manufacture", lecture, London, 1938.
(11) Wenzl, Hermann, "Zellstofferzeugund mit Hilfe von Chlor", p. 73, 1927.
(12) Wingfield, Baker, Whittemore, E. R., Overman, C. B., Sweeney, O. R., and Acree, S. F., Natl. Bur. Standards, *Misc. Pub.* M124 (1936).

Limitations of Tin as a Packing Material

ALLOTROPIC TRANSFORMATION

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TIN has been found very satisfactory as a packing material for use in ordnance matériel. In certain instances rubber cannot be employed, and a material must be utilized which at least simulates some of its desirable properties. Tin possesses softness and plasticity so that it does not scratch steel but deforms readily under pressure to make a tight seal against the cylinder wall. In addition, it will not gall and is easily formed.

Tin exists in its ordinary or white form above 18° C. (64° F.). Below this temperature the gray variety is stable. The transformation, however, takes place with considerable slowness, except at very low temperatures. The rate increases as the temperature decreases until a maximum rate is reached at −50° C. The change, although slow in starting at 18° C., may be facilitated by contact with the stable form.

Gray tin is a friable substance; when the change to this form has once started, as indicated by a number of warty masses on the bright surface of the white tin, their number and size continue to grow until the whole of the white tin has passed into a gray powder. This transformation has been called the "tin plague."

That the conversion of white tin to the gray modification cannot be accomplished at will merely by cooling the specimen below the transformation point, is a known fact. Mason and Forgeng (*2*) found a temperature of −40° C., as recommended by Cohen and Van Eijk (*1*), to be ineffective over a period of 6 months on single crystals of tin. They found that tin from the same source as that used for the single crystals when cast in a cold mold transformed readily in less than 24 hours. Further investigation lead them to the conclusion that the presence of as little as 0.0035 per cent bismuth in tin, in an annealed and homogeneous solid solution, can prevent the transformation; but if the same piece is chill-cast, the transformation can proceed uninhibited along the practically pure tin in the interior of the cored crystals which exist in the chill-cast specimen.

Tammann and Dreyer (*3*) consider bismuth the most effective of common metals in inhibiting the transformation. They found 0.1 per cent bismuth necessary for more or less complete protection against transformation to gray tin.

In an effort to determine the amount of time necessary to induce the transformation of white tin to gray tin, without initial inoculation, the writers made several attempts which are summarized in the table which follows.

Allotropic transformation will take place in both annealed and chill-cast commercial tin. Although slow in starting, it progresses rapidly at ordinary winter temperatures. A small amount of such transformation on the bearing surface of a tin packing would cause leakage. Since a perfect seal must be maintained at all times in hydropneumatic mechanisms, the relative ease of transformation precludes the use of pure tin as a packing substance in ordnance matériel. Tests of 0.1 and 0.5 per cent bismuth in tin indicate that even these small amounts of bismuth will increase the hardness and decrease the elasticity to a marked degree. Since softness and plasticity are the desirable properties for packings, the addition of bismuth would defeat the purpose for which the packing is intended.

Test No.	Shape, Inch	Treatment		Change
		Temp., ° C.	Time	
1	0.25 round	−45	3 days	None
2	0.312 round	−35	3 days	None
3	0.25 round	−25	3 days	None
4	0.312 round	−18	3 days	None
5	0.006 sheet	−45	3 days	None
6	0.006 sheet	−35	3 days	None
7	0.006 sheet	−25	3 days	None
8	0.006 sheet	−18	3 days	None
9	0.25 round	+5	8 mo.	None
10	0.312 round	+5	8 mo.	None
11	0.006 sheet	+5	8 mo.	None
12	0.0625 sheet	+5	2 mo.	Gray tin formed[a]

[a] This sample was partially submerged in an electrolyte of ammonium stannous chloride.

After the failure to produce a change to gray tin in this short time except by immersion in ammonium stannous chloride solution, other samples were prepared for further tests. Two grades of tin were used. One was a commercial grade and the other was Bureau of Standards sample 42B prepared for melting point determinations. Chill-cast and annealed samples of each were prepared. They were placed in a container suspended in the brine tank of an ice manufacturing plant for one year. The temperature of this brine was approximately −10° C.

At the end of this time, there were a few dark spots on one or two pieces which were assumed to be gray tin. Six of the samples were scraped smooth and clean, and a small amount of the gray powder from the partially transformed pieces was scraped onto these clean surfaces. Scratches were made on the surface and the gray powder rubbed into the scratches. The pieces of tin were then sealed in individual glass tubes (Figure 1) to prevent contamination. The samples were returned to the brine tank and left there for 4 months. They were then placed on an outdoor exposure rack for an additional 6-month exposure to winter weather. The following samples were used:

No.	Type of Tin	Condition	Dimensions of Sheet, Inch
1	Commercial	Annealed	0.008
2		Chill-cast	0.070
3		Annealed	0.070
4	B. of S. 42B	Annealed	0.008
5		Chill-cast	0.070
6		Annealed	0.070

At the end of the winter when they were again examined, transformation had taken place on all the specimens. The greatest amount had occurred on sample 1. Figure 2 shows that in spots the transformation had proceeded entirely through the sheet which is approximately 0.008 inch thick. One of the larger areas where the transformation had progressed through the tin is shown at the point marked by the arrow.

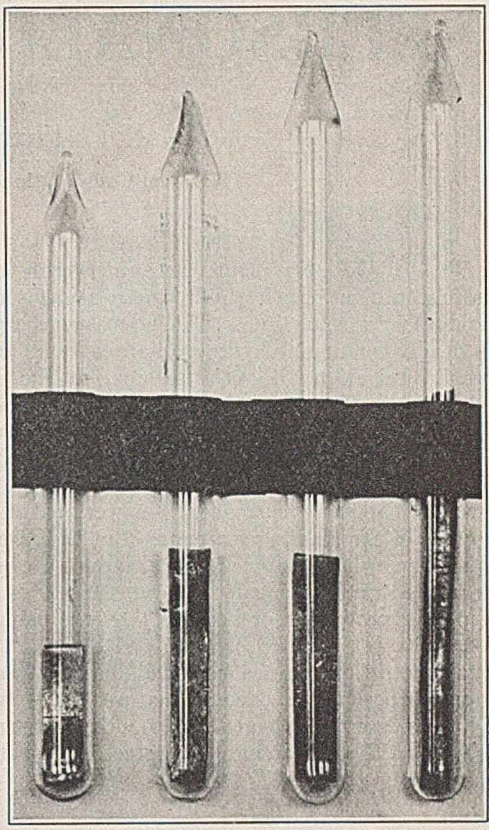

FIGURE 1. SAMPLES OF TIN UNDERGOING ALLOTROPIC TRANSFORMATION

Slight transformation had also taken place on the inoculated surfaces of samples 2 to 6, which proved that the gray powder initially obtained was gray tin.

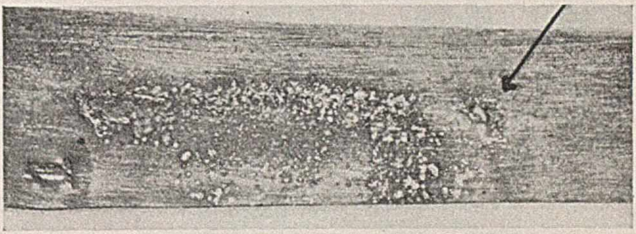

FIGURE 2. PHOTOMICROGRAPH OF TIN UNDERGOING ALLOTROPIC TRANSFORMATION (× 2)

Since some transformation was found on all samples, it was assumed that bismuth was absent. A color reaction test with a cinchonine-potassium iodide solution indicated the absence of bismuth in all samples. This finding was confirmed by spectrographic analysis.

Literature Cited

(1) Cohen and Van Eijk, *Z. physik. Chem.*, 30, 601 (1899).
(2) Mason and Forgeng, *Metals & Alloys*, 6, 87 (1935).
(3) Tammann and Dreyer, *Z. anorg. allgem. Chem.*, 199, 106 (1931).

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PERSONALIZED PROTECTION

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IN A WATER-FRONT plant where rats were a perennial nuisance, fumigation with hydrocyanic acid gas had been the practice for some time. The foreman in charge knew well the deadly quality of hydrocyanic acid and had conducted each fumigation without a mishap. In the last one, equipped with a yellow-canister mask, he was opening the windows himself from the outside when someone called to him. To answer, he lifted the mask momentarily from his face. His knees buckled and death followed shortly.

This was an actual occurrence. We were asked not to use the name of the plant or foreman. But the case has its counterpart somewhere in the chemical industry every day. Men are injured time and again, either because they are not wearing proper protection or because they are using it unsafely.

Personal protection can be provided for practically any occupational exposure of a chemical nature. It is, however, generally considered supplementary to other safety equipment. The fact that a man may be protected against certain hazards through the use of a personally worn device or garment should never be an excuse for not arranging the procedure so that there will be a minimum of dust, fumes, vapors, or splashes of liquids.

(*Top*) GASTIGHT GOGGLES FEATURING THE NOD-AND-SHAKE PRINCIPLE BY MEANS OF WHICH THE WATER IN THE CUP OF THE GOGGLES WASHES AWAY THE FOG COLLECTING ON THE LENSES

(*Circle*) WIRE SCREEN GOGGLES

Courtesy, E. D. Bullard Company

(*Bottom*) TYPICAL LIFE BELT WITH ATTACHED SAFETY LINE

Courtesy, Mine Safety Appliances Company

In clothing the chemical worker safely, three essentials should be considered:

The garment or device must afford adequate protection against the hazards to which the wearer will be exposed.

It should be reasonably comfortable and as light in weight as is compatible with protective efficiency and durability. Its weight should be carried by the part of the body best able to support it, and it should not interfere with the essential movements of the worker.

It should be durable and generally as attractive in appearance as possible, and its cost, including purchase price and maintenance, should not be greater than the job can stand.

That these requirements may be met, a careful checking of the chemical hazards of a plant and their probable effect on the health of each employee is necessary. A program may include the following items:

A thorough study, from the viewpoint of accidents and health, of all processes in the plant.

A check of each employee at the time of his employment, to determine as far as possible the degree of individual susceptibility to the hazards in question.

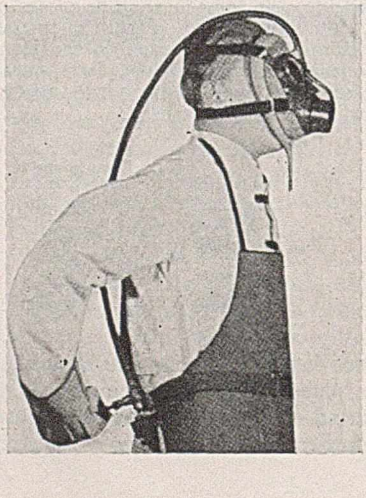
A continuous study of the adaptation of each worker to the hazards of his work.

Insurance companies report many cases of dermatitis and other unsatisfactory developments because employees in chemical plants frequently fail to have their clothing washed or to bathe regularly.

Protective clothing means, first of all, clean clothing. Some firms supply outside work garments and have them returned at necessary intervals for proper laundering. Others even go so far as to provide underwear so that they may insist on daily baths for employees. In these plants double lockers are provided for each man so that street clothing may not be soiled or odorized by proximity to work clothing.

Hats, Helmets, and Hoods

Under some conditions it is desirable to protect the head, neck, and shoulders of workmen against spills and splashes of corrosive liquids. A broad-brimmed felt or rubber hat is useful in protecting against dripping from overhead. If the crown is reinforced, it will also protect against falling objects. "Hard" hats, while not used to any extent in the chemical



ADJUSTING THE AIR VOLUME FOR A FACE MASK BY MEANS OF SMALL VALVE LOCATED ON THE BELT

Courtesy, Standard Safety Equipment Company industry so far, are light, serviceable, and practical for many operations.

Helmets, face masks, and hoods are designed for many purposes where the face must be protected. A shield used rather widely in the chemical industry is made from a sheet of cellulose acetate. This is mounted on a frame of light metal, such as aluminum, allowing wide visibility. The shield is attached to a headband. Shields can be made or purchased for many different jobs. Hoods are for working in gases which may affect the skin, so that the head and neck must be covered. Each job should receive special consideration.

Goggles

Saving eyesight has long been a part of industrial accident-prevention work. That the necessity for the use of goggles is not yet fully recognized, however, is indicated by the fact that each year in the United States there are more than 300,000 industrial injuries to eyes, each resulting in at least one day of disability. In 2000 of the cases there is complete loss of vision in one or both eyes. The total loss of time from work because of eye accidents has been estimated at 3,600,000 days annually, and the total loss in compensation and medical bills is some $50,000,000.

A typical case is that of a man who was working at an acid vat and had on a pair of coverall safety goggles. When questioned as to why he wore them, he replied that he had ruined a pair of 10-dollar spectacles before he started wearing goggles. The acid had pitted the lenses. When asked whether he had worn goggles before he had had to buy glasses, his answer was "No." This man valued a pair of 10-dollar eyeglasses more than his own eyes.

Goggles are of interest to the chemical industry not only as protection against the larger flying objects, but also against splashes of hot or corrosive materials, such as strong acids or alkalies, and against dust clouds. In some cases where the exposure is only to a light acid mist, closely fitted cup goggles have been used. Where there is danger from a spray or splash, goggles with a rubber frame, fully enclosing the eyes, should be worn. Only a small amount of acid is necessary to cause a severe eye injury.

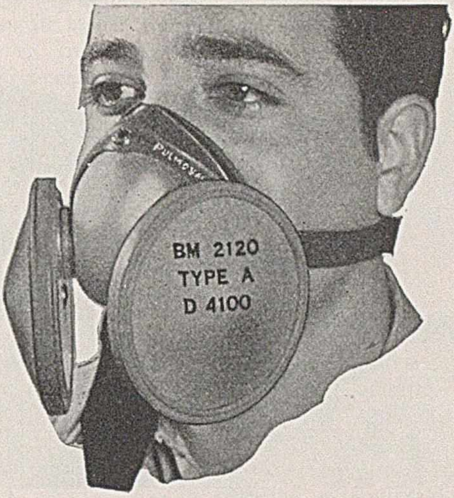
Even in the laboratory it should be a rule that every person doing gas analysis where combustion might be involved must wear goggles. It is not at all uncommon for glass combustion pipets or other laboratory equipment to explode and send sharp particles in all directions.

If it is necessary to keep dust out of the eyes, specially designed goggles, available commercially, can be secured. Only goggles with optically perfect lenses which conform to American Standard Code specifications should be used.

On some operations special types of eye protection may have to be devised. One concern fits a dummy with goggles at which water is thrown from different angles and even squirted directly into the ventilation louvers to determine whether effective protection is being provided. In addition, experimental goggles are distributed to different workmen so that the practical benefit of their reactions may be obtained. As a result of these tests and experiments, the safety engineer may determine which type of goggle best offsets the hazards of the job. Care must be taken, however, not to make experimental "guinea pigs" out of employees by asking them to try out inferior protection on hazardous work.

Goggles are sometimes ineffective because moisture adheres to the lenses and impairs vision. This problem was solved in one instance by providing a mask of fine bronze mesh for the face. Reasonably good vision was available and yet, because of the fineness of the screen, splashes from the tanks were prevented from reaching the goggles, or other parts of the face. Screen goggles are used on many jobs for protection against splashes of molten metal.

Fogging of goggles on operations where steam or vapors are encountered may be controlled by various commercial compounds for coating the lenses and keeping the goggles clear for a limited period of time.



Courtesy, Pulmosan Safety Equipment Company

Double-Filter Respirator Allowing Unobstructed Vision

The best fitting goggles will not always prevent some part of a heavy splash on the forehead from running down behind the goggles into the eyes. Should the operator keep his eyes tightly closed, injury from the corrosive liquid may be controlled and vision saved. The usual tendency is for a man to open his eyes in an attempt to find a fountain or shower by which his eyes may be flushed, and before he has sufficiently diluted the corrosive liquid with water, permanent damage been done. This is a matter of education to be considered in many chemical plants. Men should be instructed to keep their eyes tightly closed when splashes strike the face and call someone to assist them to a fountain or shower where the eyes can be effectively flushed. At times suitable hoods may preclude the possibility of such accidents.

Another exposure against which eyes need protection is that of radiant energy. In the case of ultraviolet radiation, as found in electric welding, long exposure results in serious burning of the skin. Impairment of vision through the absorption of an excessive amount of heat energy (infrared rays) is a possibility, although it is not certain that the eye is more subject to injury from this source than any other part of the body. Excessive brightness is a third source of danger and discomfort. Specially colored lenses or colored glass screens are necessary for protection against hazards of this nature, as is a shield to protect the face.

Many goggle manufacturers are now supplying goggles with tempered, shatter-proof, and prescription-ground lenses. Additional cost is slight, and the lenses are much more suitable under many situations.

Respirators

Much progress has been made in the development of respirators, especially following the impetus received through the need for protection against poisonous gases during the World War. The use of respiratory protection, however, still involves some misunderstanding, and serious injuries can result through missuse.

Mechanical filter respirators give protection against particulate matter, such as silica dust and fumes of zinc, lead, etc.

Respirators should be chosen for comfort to the wearer, for efficiency as a filtering or cleansing medium, and for the ease with which air can be inhaled and exhaled. Equipment that holds exhaled air inside of the face piece causes a rapid rise in fatigue, and it is advisable that a respirator be fitted with a check valve. As far as possible, only those pieces of respiratory equipment which have received official approval from the United States Bureau of Mines for the particular purpose they are intended to serve should be used. (A list of approved devices and their manufacturers may be obtained upon application to the bureau.) However, for protection against the nontoxic or purely "nuisance" dusts, such as lime dust or soap powder dust, some authorities believe that the lighter weight and lower resistance mechanical filters have a definite place. Some filters fail to meet the requirements of the United States Bureau of Mines, not because they fail to remove fumes but because they offer resistance to breathing. In the use of mechanical filter respirators, it must be remembered that they are of no value in an atmosphere deficient in oxygen, nor where protection must be afforded against a gas or vapor. Neither will any respirator prevent a poison from being absorbed through exposed skin.

Courtesy, Willson Products, Inc.

FILTER (*left*) AND BAG (*right*) RESPIRATORS FOR PROTECTION AGAINST FIBROSIS-PRODUCING DUST SUCH AS SILICA, QUARTZ, ASBESTOS, ALUMINUM, ETC.

Gas Masks (Canister Type)

In many instances gas masks are considered as emergency protective equipment only. Wherever operations which expose employees to dangerous gases can be so rearranged as to make masks unnecessary, except perhaps when there is a leak or break in a closed system or container, the revision should be made. There are cases, however, where gas masks are considered as regular operating equipment.

In one well-designed chlorine plant, for instance, workmen have small chemical respirators hanging constantly from straps around their necks. In filling and opening tank cars containing liquefied gases of an injurious nature, it is common practice for a workman to carry or wear a gas mask. They are part of the personal equipment, too, in gaging oil tanks that contain high-sulfur petroleum as well as in other operations where a workman has occasion to mount tanks filled with harmful materials. In the cleaning of tanks and vats, masks are used widely as regular operating equipment.

Where unknown gases may be encountered or a number of different hazardous gases are present, a canister that will give protection against all gases, including carbon monoxide, is necessary. This canister is provided with filtering and absorbing media for a number of gases. If, however, the particular gas or combination of gases to be encountered is known definitely, and there is no possibility of other harmful gases in the vicinity, a canister designed for the particular exposure is advisable; care must be taken, of course, always to select the right canister. A canister filled with an absorbing medium for a single gas will last much longer than one of the same size filled with various absorbing agents. Where such masks are used, it is good practice to discard the canister after each use. The re-use of canisters is recommended only when the concentration of the noxious gas is known and a system is followed whereby masks are issued by one person and a careful record kept of the time each canister has been in service.

Canisters are usually good for less than 10 minutes of further service once the odor of contaminated air has come to the user's nostrils. It is recommended, however, that a person withdraw from contaminated air immediately upon noting its presence in the facepiece. He should then ascertain that the dangerous gas is not coming into the facepiece because of poor fit or adjustment which can be readily corrected by tightening the straps. In the case of carbon monoxide, where no odor is present, a person must depend upon his knowledge of the service time of the canister as a basis for making necessary changes. Most carbon monoxide masks are equipped with timers.

One night when a worker in a pulp mill came on the job, he discovered the presence of chlorine gas in the air. He put on a gas mask, pulled the straps, and went into the bleachery to shut down the pump. While absorbed in locating the trouble, he got a strong odor of gas and quickly made his way outside. As the mask was removed, the man started coughing. He was sent home, where he was visited by a doctor and advised to stay in bed for a week as a precaution against pneumonia.

After this accident two possible causes were found. The mask had not been fitted properly so that gas leaked in under the face plate, and a heavy growth of whiskers on the man's face was somewhat responsible for this condition. Furthermore, the canister had already absorbed a high concentration of gas and offered very little protection. Either of these causes could have been responsible for the man's death.

It is best to store masks in permanently located cabinets, clearly marked for emergency use. That no mask should be returned to the cabinet after use until it has been serviced by the person in charge of such equipment, reconditioned, and made ready for the next user, is obvious. Frequently the atmosphere in a chemical plant will be so corrosive that it may be difficult to maintain masks in good condition. A practice sometimes followed is to seal the masks in paper bags which are then coated with paraffin. This practice not only keeps masks in good condition but also provides an excellent method for checking their use, inasmuch as a mask cannot be used until the paper bag is broken.

In some plants gas masks are located in cases placed on the outside of the building or at some other convenient place apart from a location where corrosive gases may be present. The cases can be made tight and closed with a glass panel to be broken with a small mallet attached to the box, when an emergency occurs and the mask is needed.

A canister, even though not used, will not last indefinitely and should be replaced after the period of time recommended by the manufacturer. Canister masks will not be effective where there is a deficiency of oxygen or where the concentration of noxious gas exceeds the safe limit named by the mask manufacturer.

Hose Masks

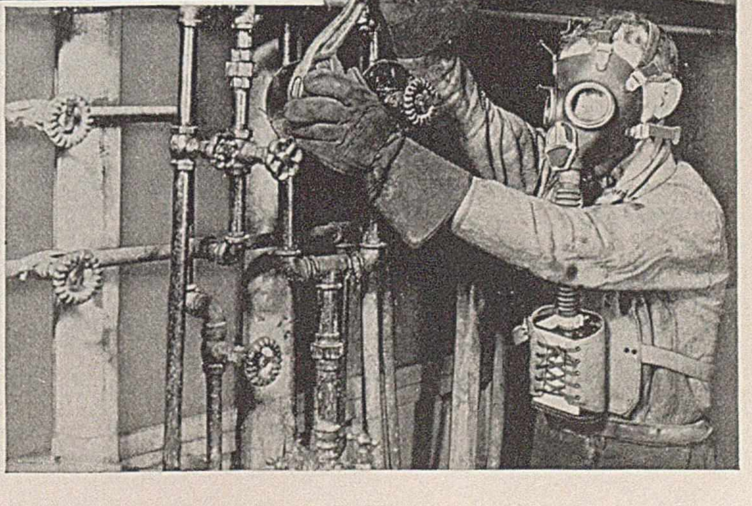
The hose mask, frequently a positive pressure mask, is the best type of respiratory protection for many applications. It is cumbersome, however, and the length of the hose limits the distance the wearer may travel. There is no chemical reaction in a hose mask because the air is taken from a point outside of the danger zone. This mask is satisfactory in atmospheres lacking oxygen. This equipment is recommended particularly for work in tanks and other confined places containing heavy gases not readily displaced by air.

For spray painting and other operations difficult to ventilate, positive-pressure masks are usually recommended, since they give protection not only from the vapors of solvents but also from the particles of pigment which fly through the air. Small respirators with chemical cartridges, however, may give satisfactory protection in many situations from both vapors and paint mists. In some painting operations there are no harmful vapors, and protection is required only against the mists, which are essentially particles; for this work a mechanical filter may be satisfactory.

The amount of air supplied to an air line respirator is very important. If it does not exceed the quantity inhaled by a person at the instant of greatest intake during the respiratory cycle, some outside air will be drawn in around the facepiece or under the hood. If the quantity of air supplied exceeds this amount and a positive pressure is maintained constantly within the facepiece, then good protection can be expected and the air will contain only such contaminants as may be in the intake air to the compressor or which are added by the compressor. In some instances, however, such contamination may be considerable, and extreme care must be taken to provide a supply of air that is clean and safe to breathe. It has been pointed out that even though a positive pressure is maintained in the facepiece or hood at all times, there is a possibility of flying particles entering the facepiece through any opening, when the velocity of such particles is greater than the velocity of the outcoming air. This has been noted in certain types of sandblasting helmets and hoods.

Self-Contained Oxygen Breathing Apparatus

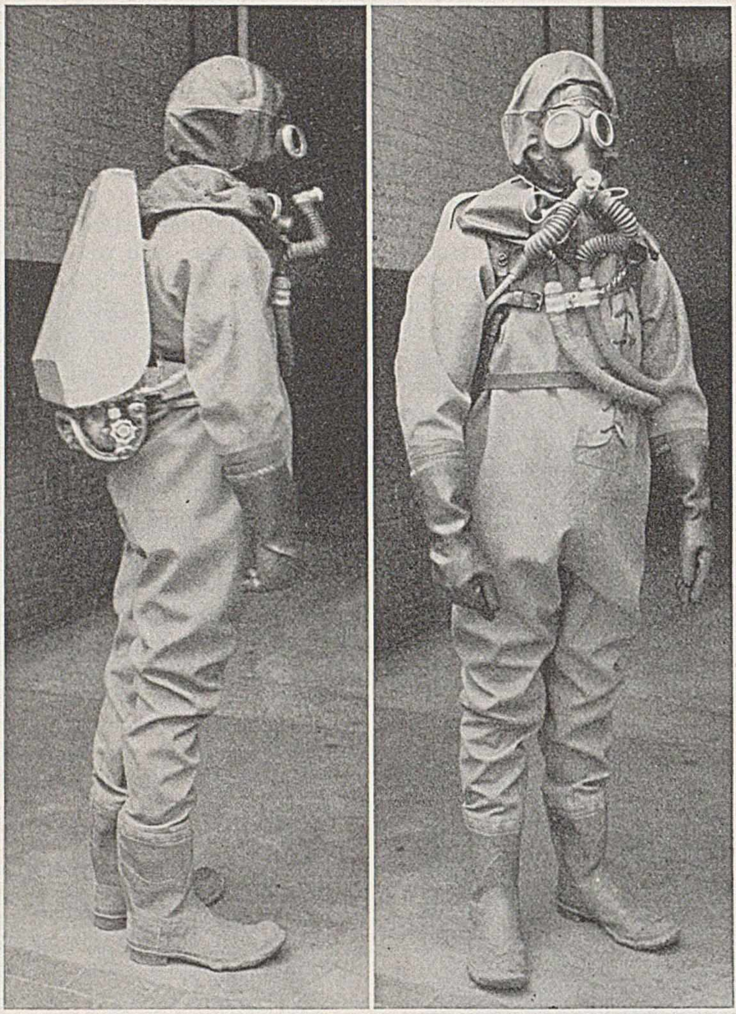
Apparatus of this nature protects against all deficiencies of oxygen and also against any concentration of dangerous gases or vapors for a limited time, except those that may be absorbed through the skin. In oxygen breathing apparatus, the wearer breathes the same air over and over, but the apparatus is equipped with a chemically filled canister which removes carbon dioxide from the exhaled breath and provides additional oxygen from a container of compressed oxygen to replace that which has been consumed. The United States Bureau of Mines does not consider a man capable of wearing oxygen breathing apparatus for rescue work until he has received the training equivalent to wearing the apparatus for 15 hours. If oxygen breathing apparatus is to be used in a plant, thorough instructions are recommended before workers



(*Top*) The Face Should Be Adequately Protected When Attending the Operation of Nitrometers

(*Center*) Gas Mask Canister Assembled with Half-Mask Facepiece for Protection against Vapors When Eye Protection Is Not Required

(*Right*) M. S. A. Bureau of Mines Approved Organic Vapor Gas Mask in Use in a Chemical Plant



Courtesy, Eastman Kodak Company

Man Wearing a 2-Hour McCaa Oxygen Breathing Apparatus with Complete Rubber Suit, Hood, and Boots for Protection from Ammonia

are allowed to go into atmospheres in which they may risk their lives should the apparatus fail.

Cleanliness

One of the important factors that give rise to chafing of the skin is failure to keep goggles, masks, and respirators clean. Margins become contaminated with salt from perspiration, oils from the skin, and dirt from the atmosphere. Facepieces of all types of protectors should be scrubbed with soap and water at the end of each day of use and before being reissued to other employees, to keep them in a sanitary condition.

Directions for cleaning may be procured from the manufacturers. Those issued by the American Standards Association are:

> Subjection to a moist atmosphere of antiseptic gas, such as formaldehyde, for a period of 10 minutes.
>
> Immersion in boiling water for 5 minutes.
>
> Immersion for 10 minutes in a solution of formalin made by dissolving 1 part of 40 per cent formaldehyde in 9 parts of water.
>
> Immersion in live steam for 5 minutes.

The odor of the disinfectant should be completely removed from gas masks so that it will not prevent the wearer from detecting the first traces of a dangerous gas coming to his nostrils. Canisters should be attached to facepieces only when all signs of moisture have disappeared.

If respirators are to give maximum satisfaction, they require constant care and conditioning to assure the breathing efficiency of new equipment. Masks of all types should have periodical inspection.

Facepieces generally must fit snugly, and because of this they sometimes chafe the skin. In a lime manufacturing plant considerable difficulty was experienced with skin irritations on the face at the point where respirators made contact. The situation was relieved through the use of a protective emollient, such as vaseline, applied to the face before a facepiece was put on. In this instance the skin trouble was completely eliminated. The irritations had been caused by the blending of lime dust with perspiration on the face. Similar good results may be obtained by applying an emollient on the neck where the shirt collar may rub.

Before protective respiratory equipment is purchased, the manufacturer should submit information indicating the purpose and efficiency of his product and by what laboratories it has been approved. Authoritative information on face and head protection is available at the headquarters of the American Standards Association (*1*). Further information on respiratory protection is given by Drinker, Yant, etc., (*2*).

Clothing

Many articles of protective clothing are made of rubber or a composition of rubber and other materials. Garments of this kind offer protection against acids, fumes, and vapors and in operations involving the use of moisture or liquid. Rubber goods are manufactured also for protection against electrical hazards, but generally coverings made specifically for chemical protection are not heavy enough to give adequate protection against electrical currents. Rubber boots, overshoes, gloves, sleeves, coats, hats, and blankets constitute some of the coverings in which rubber is an ingredient. Men working at acid tanks or pickling vats should generally be equipped with acid-resisting rubber boots, aprons, gloves, and other rubberized garments. Aprons usually reach well below the workmen's knees, and the boots reach to the hip. Boot tops should never be left open; dangerous liquids may run down inside. There is also an acidproof rubberized suit on the market which resembles a coverall with drawstrings at the neck, at the sleeve cuffs, and at the ankles. A suit of rubber pants, coat, hooded helmet, rubber gloves, and boots is valuable for inspecting or cleaning tank cars, tanks, and other vessels which may still contain traces of corrosive substances after being cleaned.

Here, again, protective clothing may not be sufficient in itself. Before a man is allowed to enter a tank, all supply lines should be blanked off so that acids or other materials cannot flow into the tank. The tank should then be cleansed thoroughly with steam or by some other approved method. If flammable gases may be present, nonsparking tools of nonferrous metals should be used while working inside. Special explosion-proof lights should be used also. The cleaning of tanks should be carried on only under thoroughly qualified supervision.

An accident indicating the need for protection of workers' clothes happened in a cresylic acid plant. A splash occurred from one of the tanks, and a man's trousers became saturated with a dilute solution of the acid. This man had but one pair of trousers at the plant so he wore them home, saturated with acid. As the result of the prolonged contact with his skin, there was a severe burn.

Where men are exposed to harmful materials, they should wear clothes kept in good condition with collars buttoned and shirt sleeves rolled down. The head also should be covered properly.

Gloves

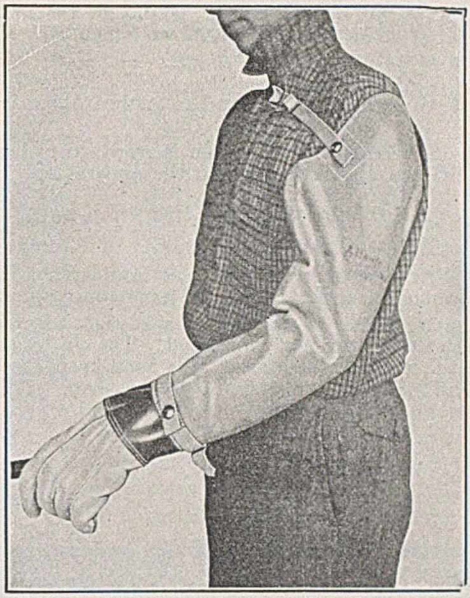
Rubber gloves or mittens are commonly used when handling caustics, acids, alkalies and other materials which may be injurious to the skin. Sometimes it is necessary to perform work on objects which have a rough exterior and in contact with which the rubber would wear very quickly. Under such circumstances the rubber gloves may be protected by an overglove of leather which will afford greater resistance to punctures and cuts and provide better protective qualities.

It is sometimes a problem, however, to find a glove which is sturdy enough to stand hard usage and yet pliable enough to permit free use of the hands and fingers. In handling objects, gloves may prove clumsy inasmuch as they destroy the sureness of touch or become slippery and are often a cause of objects being dropped on the legs or feet.

Gloves should be long enough to come well over the wrist and under the shirt or coat sleeve. There should be no gap of exposure at the wrist. Long, flaring gauntlets are picturesque but hazardous. Not only will they catch in machinery, but they may also catch dangerous materials and conduct them to the hands and fingers.

A leaky rubber glove is likely to be the cause of serious injury; therefore, gloves used in strong alkalies or acids should be tested frequently. Because of the nature of the solvents to which workers are sometimes exposed, rubber gloves may not be practical. The use of a protective paste in such cases may answer the problem.

Soiled glove interiors will cause skin irritations. In one plant where the use of protective rubber gloves was necessary, considerable difficulty was experienced in keeping the inside clean and free from acid solutions. A hand-shaped form was made from small pieces of perforated brass pipe. The glove could be slipped over this form and water turned on which completely flushed the interior, even to the tips of the fingers.



Courtesy, American All-Safe Company, Inc.

SPECIAL HAND, WRIST, AND ARM PROTECTION AGAINST HEAT, ACIDS, AND CAUSTICS

In this way the interior was kept clean, deterioration was arrested, and workmen received satisfactory protection. Turning gloves inside out, washing with soap and water, and drying is, of course, effective.

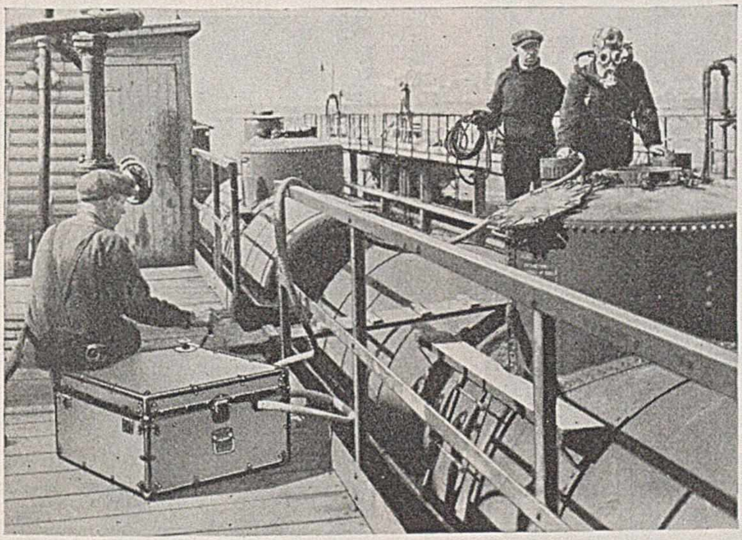
Shoes and Leggings

It has been estimated that 24 per cent of all industrial accidents are to the legs and feet, and that 20 per cent of workmen's compensation payments is for foot and leg injuries. Protective devices for the prevention of these injuries are shields, spats, leggings, boots, overshoes, special soles, and hard-toe shoes.

When exposed to splashed acids, hot liquids, or molten metal, "Congress" or other types of shoes which have no lacer openings and may be removed quickly are desirable. Shoes with wooden soles and leather uppers may be used to advantage. Canvas or leather leggings or spats are frequently employed where hot metals or other liquids must be handled. Leggings used around hot substances should not have projecting clasps, wrinkles, etc., where liquids may lodge and burn through to the flesh. Leggings should be provided with suitable flares which cover the tops of the shoes and be quickly removable.

In plants where men are likely to get acid on their feet or legs, tubs of water are sometimes supplied. Illustrating the value of this is a case where a man opened the ash-pit door of a furnace under a leaky still, and acid poured out over his feet. He jumped into a large tub of water within a few feet of the place the accident occurred, and as a result he received only minor burns.

Shoes with heavily reinforced toes are available and are as comfortable and good looking as those of the nonsafety type. Safety shoes



MAN WEARING A BUREAU OF MINES APPROVED COMBINATION HOSE MASK ABOUT TO ENTER A TANK CAR

The helper holds the lifeline attached to the mask safety belt. Fresh air is supplied the wearer by means of the hand-operated blower.

(*Right*) Skull Guards Protect Drillers in Every Important Oil Production Field

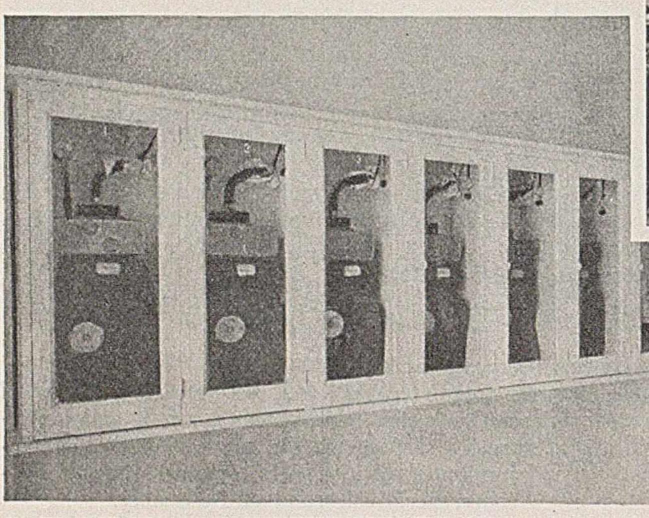
(*Center*) A Good Way to Store Breathing Apparatus When Not in Use

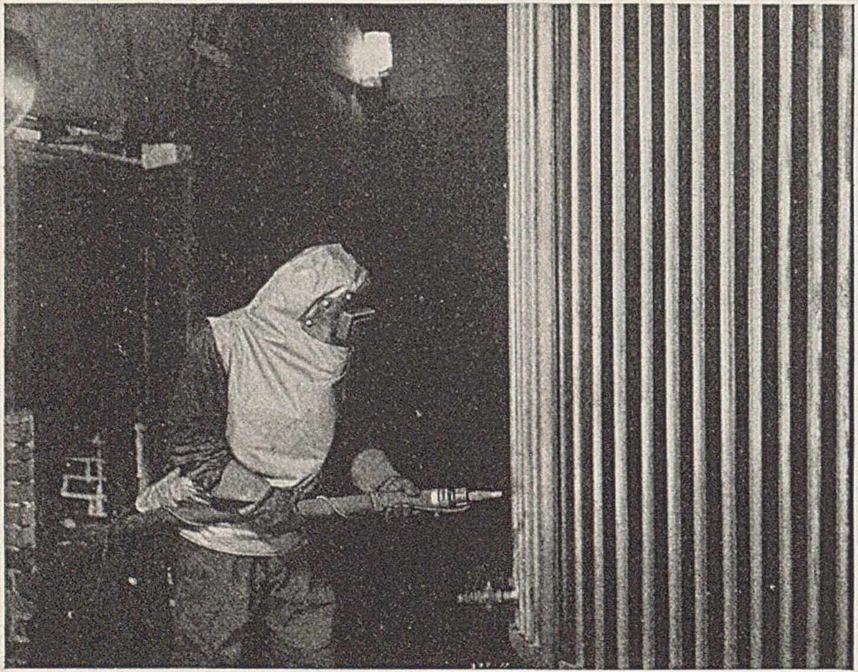
The cylinder of compressed oxygen is ready to recharge individual oxygen bottles on the apparatus.

Courtesy, Ford Motor Company

(*Bottom*) Sandblaster Wearing an Abrasive Mask While Blasting a Large Transformer

Clean compressed air is supplied to a gastight facepiece underneath the light weight latex hood. The air exhausting from the facepiece underneath the hood keeps it cool and makes it more resistant to abrasives.





Courtesy, Industrial Products Co.

Acid Suit and Hood

have saved thousands of foot injuries. Many employers keep a stock for sale to employees; in some instances a local shoe merchant has set up a branch in a plant, where a clerk is kept part time to sell shoes and see that they are fitted properly in each case.

Workers who must wear rubber boots are advised to use heavy woolen socks, since they increase comfort and have no effect on the circulation of the blood. Additional comfort may be secured by wearing a second pair of light-weight cotton socks under the wool ones.

Another problem is the best method for keeping the interior of rubber boots clean. Generally each worker should have his own equipment. However, these need to be sterilized periodically, and this can be done effectively only at the plant. Care must be exercised in such cases to see that boots are returned to their rightful owners.

Safety Belts

In the case of safety belts much local ingenuity has been exercised, although there are many good safety belts on the market. In one plant where there are a large number of tanks, tank cars, vats, and other vessels which constantly need cleaning, a simple belt has been devised with a substantial iron ring riveted in the back of it, to which a rope is attached. This permits the cleaner or painter to do his work unhampered by a heavy uncomfortable belt, and also makes certain that he is taken from the tank immediately by a helper standing outside if he should be overcome with noxious vapors or gases. For special jobs, special belts are often necessary. Belts made of fabric which has been treated to withstand corrosion and deterioration by chemicals to which they will be exposed are available. This equipment should be tested and approved by some reliable laboratory before dependence is placed on it as a life saver. Where there is danger of falling, it is well to use some device to absorb the shock on the belt, both to keep the belt from breaking and to prevent injury to the man. The use of ropes on safety belts where acid is present presents a distinct hazard, since the strength of rope may be quickly impaired. An acid-resistant chain or cable should be used.

Fire risk in industrial establishments, in so far as it relates to structural conditions, has been stressed again and again. However, probably less attention has been paid to processing methods and operations which have caused many fire tragedies.

In one case in New Jersey a laborer was employed in feeding dye substances into a small pulverizer when the mixture flashed back and his clothing caught fire. The terrified man ran through the plant a mass of flames until other workmen caught him, rolled him on the floor, and smothered the fire. Five days later he died.

In another case, a worker was fatally burned in a plant where insulating material was manufactured. In the coating process, the material was being run through a batch of liquid which consisted of pitch, varnoline, kerosene, linseed oil, and other ingredients. The deceased was wearing clothing that had been stained with the material. A spark caused surrounding vapors to flash and ignite the man's clothing. In this case, again, the burning clothes were the factor which led to his death. Many similar examples could be cited.

Three materials—leather, asbestos, and flameproof duck—are used in the manufacture of most garments for protection against heat. Flameproof duck is the cheapest of the three and is suitable where there is not a long exposure to a high temperature. Asbestos is used also in the manufacture of garments for protection against flame. Since asbestos is not a good heat insulator, there should also be insulation such as a wool lining. A good grade of asbestos is absolutely fireproof, although a small percentage of cotton used in its fabrication will generally oxidize without the danger of direct combustion.

Leather used in protective clothing is usually either horsehide or cowhide. Oil is used in tanning leather; although it is necessary to retain a certain amount of the oil, if too much has been used, leathers employed near hot operations may deteriorate rapidly. It has been estimated, nevertheless, that a leather legging will outwear three duck leggings and probably almost as many of asbestos. This same comparison exists for gloves. Leather provides good general-purpose protection, except where its weight may be an objection.

(*Top*) A RECENT DEVELOPMENT IN OXYGEN BREATHING APPARATUS
This man is well equipped for rescue work with his safety hat and electric lamp.

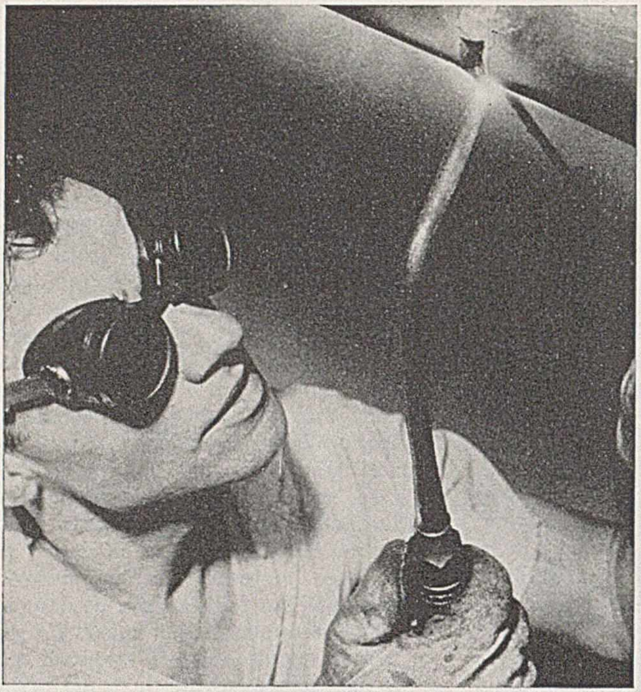
Courtesy, U. S. Bureau of Mines

(*Center*) REFILLABLE MOUTHPIECE MASK FOR USE IN LIGHT CONCENTRATIONS OF ACID GASES

Courtesy, E. D. Bullard Co.

(*Bottom*) A WORKER EQUIPPED WITH A FRESH AIR HOSE MASK

Courtesy, Davis Emergency Equipment Company



Courtesy, Linde Air Products Company

Dangerous Light Rays, Flying Sparks, or Bits of Hot Metal Cannot Cause Trouble If the Operator Has His Eyes Properly Protected

Felt is used in some types of protective clothing where there is exposure to excessive heat and where the use of duck, asbestos, or leather is not desirable. In one instance a concern having electric furnace operations uses felt to make protective jackets and trousers for its furnace operators. Felt is a good protective material, is comfortable to the wearer, and is relatively low in cost. Pure wool felt has low heat conductivity, and, while it will burn, it does so slowly and without flame.

Special Exposures

Frequently in chemical plants and laboratories the development of a new process or the handling of a new chemical will make some new type of protective clothing necessary. Workers in the manufacture of fuming sulfuric acid, for instance, have been faced with this situation. As far as is known, no clothing will satisfactorily protect employees against splashes of this acid. Many companies provide only emergency showers operated by quick-acting platform valves, from which may be obtained an abundance of clean water to flush the acid burns immediately. Woolen clothing seems to be the most satisfactory protection found so far, and rubber gloves have been used with some success. However, a rubber glove will last probably less than 2 minutes when covered with or immersed in fuming sulfuric acid.

Despite the remarkable progress being made in personal protective equipment, there will always be some lag in its design and manufacture, as this industry must follow the developments in others. Protection for workers in a new process cannot generally be provided until the nature of its hazards is known. It will therefore be an advantage if employers in the chemical industry will take into their confidence designers of protective devices when new processes are in the making, so that when the work goes into production, employees may not have to wait for necessary protection.

In one instance, after a woman operator had been burned, a manufacturer was asked to provide a suitable nonflammable garment. No other specifications were given. The work, however, involved contact with electrical equipment and sometime later there was a shock injury. In the investigation that followed it was found that the salts used in fireproofing made the clothing electrically conductive.

The lag in design, however, is probably small when compared with the lag on the part of industry in accepting and putting protective equipment to use. Protective device manufacturers are as alert as possible in anticipating the needs of industry and developing new products. In marketing their equipment they frequently have to do a great amount of missionary and educational work to get reasonable distribution.

Protective clothing is sometimes uncomfortable, and mandatory use should be limited to situations chosen after careful consideration and discriminating judgment. When it has been decided that protective clothing is necessary, then supervisors must insist that it be worn, regardless of the attitude of any chance-taking employees. It is better for a workman to wear clothing specially designed for his job than to expect partially worn-out street clothes to fill the need, as is so frequently the case.

It is axiomatic that chemical equipment must be so designed that there will be no escape of harmful substances, but even in the best designed plants things happen that were not intended. It is for these emergencies generally, and for those jobs where safety design has not yet developed to a point that permits workers to proceed with comfort and safety, that personal protective equipment is designed. It is not recommended that personally worn protection in any case take the place of other safety measures.

Literature Cited

(1) Am. Standards Assoc., "American Standard Safety Code for the Protection of Heads, Eyes and Respiratory Organs", New York, 1938.

(2) Drinker, Phillip, *Mech. Eng.*, March, 1936; Yant, W. P., U. S. Dept. Labor, *Bull.* 21, Pt. 2 (1938); Natl. Silicosis Conference Rept. on Engineering Control, pp. 29–48 (1938).

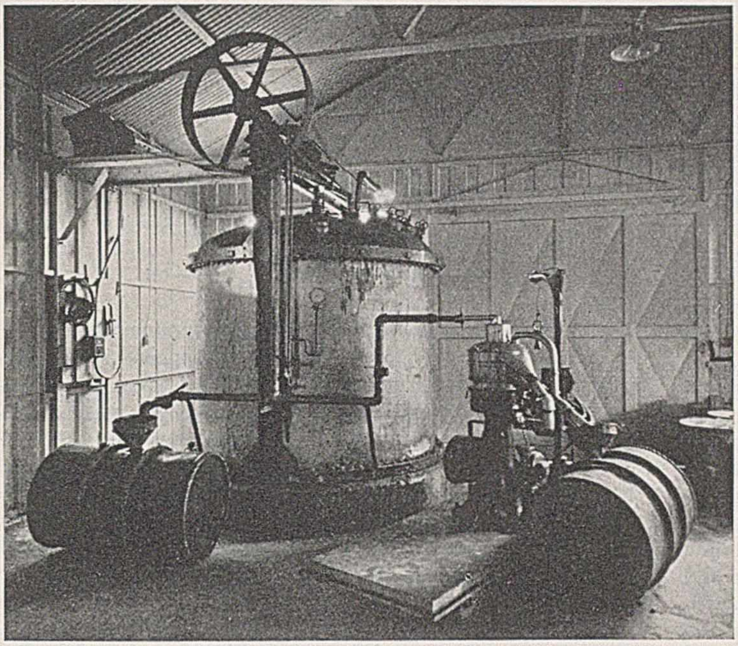
Photo by Cy La Tour

Preparing to Enter a Dangerous Atmosphere

Urea-Formaldehyde Film-Forming Compositions

Structure of Water-Soluble Resins and Stability of Urea–Formaldehyde–Ethylene Glycol Condensation Products[1]

T. S. HODGINS and A. G. HOVEY
Reichhold Chemicals, Inc., Detroit, Mich.



Pilot Plant for Water-Soluble Urea-Formaldehyde Resins

The reactions of urea and formaldehyde in aqueous media are briefly reviewed in order to lead up to a study of the structure of the resinous product; the discussion is substantiated by gelation experiments.

Stable aqueous resin solutions are formed from certain compositions of urea, formaldehyde, and ethylene glycol, which comprise a definite area of a triaxial diagram of these three components.

Urea-formaldehyde resin solutions prepared in aqueous media have long been used as the basis of molding resin compounds and may, in this sense, be regarded as film-forming solutions. However, the purpose of this paper is to discuss water-soluble urea-formaldehyde resin solutions from the standpoint of film-forming compositions to be applied as a surface coating. In the manufacture of molding compounds, two alternative methods are used: A water-soluble urea-formaldehyde resin is used as the impregnating compound for the wood flour, cotton flock, alpha-cellulose, or other filler; or the filler is present in the initial reaction mixture.

Urea-formaldehyde resins have always been characterized by light color and rapid development of hardness by relatively low-temperature baking schedules and, therefore, have found widespread use as plywood adhesives, laminated wood products, paper coatings, fabric stiffeners, etc. Their use in such products is already very large, but one of the chief obstacles to their further progress has been the lack of package stability.

Without ignoring the early work done by Goldschmidt (*10*), Einhorn and Hamberger (*7*), and Dixon (*6*), the first recorded description of resinous products formed from urea and formaldehyde is given by John (*16*). John saw clearly the wide, practical possibilities of urea-formaldehyde resins, for he not only proposed them as ingredients for molding, but also as adhesives, bonding materials, impregnating media, and coating compositions. In spite of the anticipation by John that, because of their light color, hardness, and inertness, urea-formaldehyde resins would be of value as surface coating materials, the development of water-soluble resins of this type for this purpose encountered serious obstacles in industrial use. As a result, the literature for actual surface coating applications is very meager. Among the obstacles which had to be overcome, probably the most important has been lack of stability. On standing for a period even as short as 2 weeks, most of the commonly known urea-formaldehyde resin solutions form either white precipitates or gels. In a molding compound where a gel could form around or in the interstices of fibrous fillers, the question of stability in this sense was not important.

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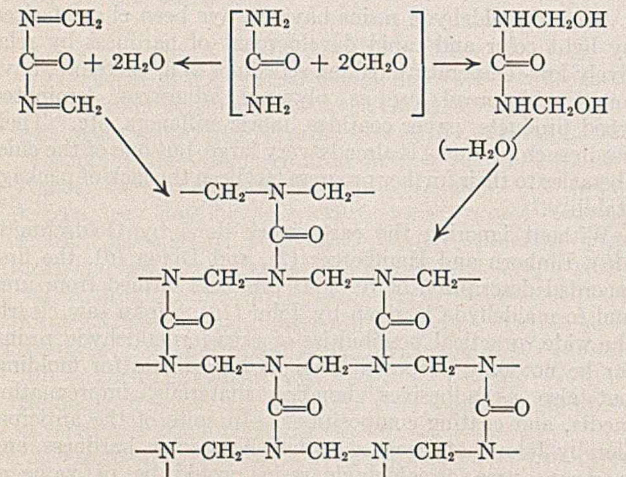
[1] The first paper in this series was published in September, 1938 (*11*).

Many efforts have been made to increase the stability of urea-formaldehyde resin solutions in water. For example, MacDonough (*19*) called attention to the effect on stability of hydrogen and other ions. He gave certain mathematical values to represent the hydrophylic and hydrophobic types of colloid. Ripper (*22*) attempted to achieve stability by controlling pH during the course of the reaction.

The authors have found that certain concentrations of polyhydric alcohols in urea-formaldehyde reaction mixtures tend to increase the stability of the resulting resin solutions and, because of this observation, made a more thorough investigation.

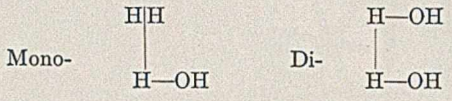
Theoretical

In a previous paper the authors (*11*) discussed certain aspects of the reactions in aqueous media. Numerous investigators seem to be more or less agreed on the general principles underlying the simple compounds formed from urea and formaldehyde—i. e., monomethylolurea when one mole of formaldehyde reacts with one mole of urea, and dimethylolurea when two moles of formaldehyde react with one mole of urea. This fundamental work goes back to Einhorn and Hamberger (*7*) in 1908. However, in the presence of dilute acids, methyleneurea, a white amorphous insoluble precipitate was reported by Hölzer (*13*) in 1884 and by Lüdy (*18*) in 1889. From either the methylolurea or the methyleneurea compound the resulting condensation product is dependent upon (*a*) the catalyst employed, including the pH of solution, (*b*) the molecular ratio of the reacting components, and (*c*) the time and temperature of the reaction. The mechanisms by which resinification progresses from the simpler initial reaction products have been discussed by many, including Staudinger (*24*), Scheibler and co-workers (*23*), Walter and co-workers (*25, 26*), de Chesne (*5*), Redfarn (*21*), Ellis (*8, 9*), and the authors (*11, 12, 15*). Whether the condensation takes place through the dimethylolurea intermediate or through the polymerization of the dimethyleneurea compound, the result seems to be the same in that a unit polymer is built up as follows:

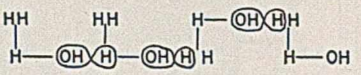


Redfarn's and Ellis' theories were discussed by the authors (*11*), and it was pointed out that neither one of these proposed theories of resin formation was tenable because no provision was made for cross linkages to account for gelation. The unit polymer as advanced in reaction 1, while not the only possibility, is nevertheless the most probable according to the chance meeting of the reactive groups in three-dimensional space when only dimethylolurea (or its equivalent) is involved. The same paper (*11*) stated that, since monomethylolurea has a potential functionality of four, it should be possible to form cross linkages between linear structures and account for heat convertibility. However, the results explained in the section on the "Polymerization of Mono- and Dimethylolurea" show that when molecules of monomethylolurea alone are involved (i. e., when the molecular ratio of urea to formaldehyde is 1 to 1), gelation does not occur.

In order to consider the possibilities and effect of the chance meeting of urea-formaldehyde intermediates, let us first represent monomethylolurea and dimethylolurea by the following symbols representing only their functional points:



Case I. All monomethylolurea:



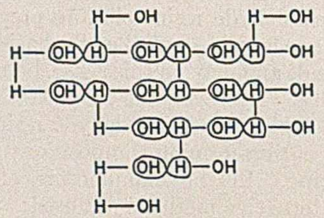
Functionality in the original reactant (monomer) (1—OH, 3—H) is 4. The result is long-chain or branched-chain polymers. Although the functionality of the system is 4,4, the 3—H does not accomplish anything more than could be accomplished if there were only 1—H acting as if the functionality were 1—OH and 1—H (or 2,2); and since there can never be more than one free $—CH_2OH$ group per polymer, independent of the length, no cross linkages can form. If no restriction is placed on the relative activity of the hydrogen atoms of the mono- compound, a branched rather than a truly linear structure will form (according to the above diagram). Cross linkages would seem possible from the high potential functionality of the system; but because of the fact that there is only one $—CH_2OH$ group per molecule and that there can never be more than one free $—CH_2OH$ group at any one time in the polymer, the full potential functionality can never be utilized. This is supported by the experimental facts in the section on the "Polymerization of Mono- and Dimethylolurea"—i. e., gelation does not occur.

The total functionality increases with degree of reaction; e. g., the monomethylolurea functionality is as follows:

	—H	$—CH_2OH$	Total
Monomer	3	1	4
Dimer	5	1	6
Trimer	7	1	8
n-Mer	$2n + 1$	1	$2n + 2$

As the structure becomes more complex (i. e., as the degree of reaction advances), the structure becomes more susceptible to the introduction of even small amounts of dimethylolurea as in case III.

Case II. All dimethylolurea:



Functionality in the original reactant (monomer) (2—OH, 2—H) is 4. The result is three-dimensional polymers with cross linkages; therefore, gelation occurs.

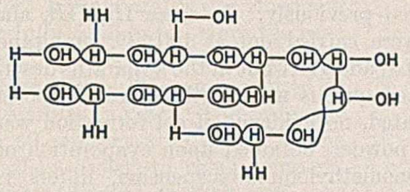
In the case of dimethylolurea, the total functionality increases with the degree of reaction (as in the case of monomethylolurea in case I), but the functionality of dimethylolurea in respect to both the reactive groups increases:

	—H	$-CH_2OH$	Total
Monomer	2	2	4
Dimer	3	3	6
Trimer	4	4	8
n-Mer	$n+1$	$n+1$	$2n+2$

Thus, a rapid gelation of this system is accounted for, because a plethora of cross linkages is possible.

The preceding structure for case II is identical with reaction 1, which results in the twelve-membered ring and the unit polymer as discussed in a previous paper (*11*).

Case III. Mixtures of mono- and dimethylolurea:

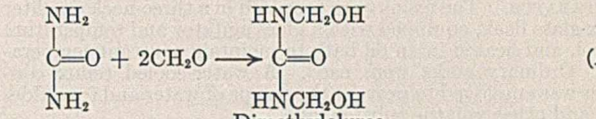


Functionality average for one mole of each monomer is $(4+4)/2$, or 4 ($1^1/_2$—OH, $2^1/_2$—H). The result is three-dimensional polymers with cross linkages—therefore, gel formation. Whenever a few molecules of dimethylolurea are present, the chances of forming cross linkages are greatly increased as compared to case I.

The above space concepts show that case II and case III forms of unit polymer are the most probable structures from the standpoint of probability of collision of the reacting groups; but, as is always true in resin formation from simpler molecules, a heterogeneous complexity of structure results. Such a resinification process is in accordance with the ideas on functionality and chance meeting of Bradley (*2*), Carothers (*3*), Hovey (*14*), and Kienle (*17*). The authors believe that the data given in the section on the "Polymerization of Mono- and Dimethylolurea" support this contention of space configuration and functionality by the evidence presented in Table I on the basis of gelation.

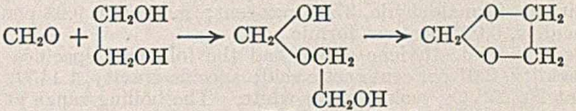
In the previous paper (*11*), the authors discussed the reaction of monomethylolurea and dimethylolurea with acetals formed from mono- and polyhydric alcohols. Many acetals were listed according to their chemical structure and physical properties. The type of final resinous product discussed in that paper, however, is hydrophobic and therefore differs radically from the hydrophylic type of acetal derivatives of mono- and dimethylolurea reaction products which are now to be discussed.

Considering the system urea–formaldehyde–ethylene glycol, according to the general formula 1 mole of urea, 3 moles of formaldehyde, *x* moles of ethylene glycol, we have the following hypothetical structural possibilities:



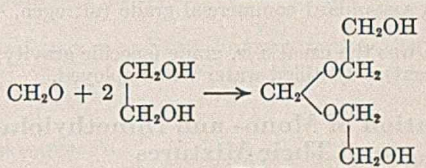
$$\underset{NH_2}{\overset{NH_2}{C}}=O + 2CH_2O \longrightarrow \underset{HNCH_2OH}{\overset{HNCH_2OH}{C}}=O \qquad (A)$$

Dimethylolurea



(B₁)

Ethylene glycol hemiformal Dioxolane (*1*, *27*)



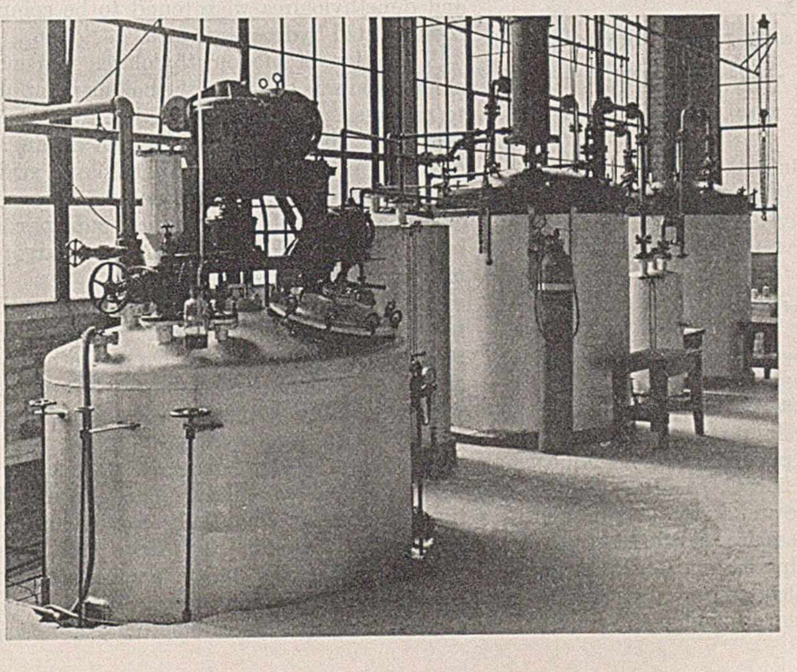
$$CH_2O + 2\begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix} \longrightarrow CH_2\begin{matrix}OCH_2CH_2OH\\OCH_2CH_2OH\end{matrix} \qquad (B_2)$$

Ethylene glycol formal

Resinification might be assumed to take place from the intermediates as follows:

$$A + B_1 \longrightarrow \text{resin composition}$$
$$A + 2B_1 \longrightarrow \text{resin composition}$$
$$A + B_2 \longrightarrow \text{resin composition}$$
$$A + 2B_2 \longrightarrow \text{resin composition}$$
$$A + B_1B_2 \longrightarrow \text{resin composition}$$

Whether the ethylene glycol enters into the reaction through the formals is questionable. The ethylene glycol



Production Kettles for Water-Soluble Urea-Formaldehyde Resins may act as a stabilizer by becoming adsorbed or orientated on the resin surface. The presence of some free ethylene glycol in the finished resin solution is possible not only by incompleteness of the reaction B_1 and B_2, but also by its regeneration by the reverse reaction when ethylene glycol formal reacts with dimethylolurea. The presence of free ethylene glycol in the final product, therefore, cannot furnish evidence as to what mechanism is involved. The work on the three-component systems is covered in the section on "Stability of Urea–Formaldehyde–Ethylene Glycol Condensation Products."

Experimental Procedure

APPARATUS. The resins were prepared in a three-neck one-liter Pyrex glass flask, equipped with a glass agitator and temperature control, and heated in an oil bath to maintain constant temperature. Ordinary corks were used. A water-cooled reflux condenser was employed to prevent the escape of water and formaldehyde and other volatile substances.

MATERIALS. The commercial formaldehyde had the following composition: formaldehyde, 37.17 per cent; methanol, 9.98 per cent; acidity, 0.027 per cent formic acid.

The commercial ethylene glycol had the following specifications: acidity, 0.01 per cent acetic acid; specific gravity, 1.1150–1.1158 at 20/20° C.; color, water-white. The boiling range at 760 mm. was: none above 210° C., 95 per cent below 202° C., 5 per cent below 195° C., and none below 190° C.

The urea was a standard commercial grade (nitrogen, 46 per cent).

The ammonia was the usual C. P. grade (specific gravity, 0.90; NH_3, 28.0 per cent). Distilled water was employed.

Polymerization of Mono- and Dimethylolurea and Their Mixtures

Many previous attempts (*9*, *21*) to explain the structure of urea-formaldehyde resins have been unsatisfactory since they fail to account for gelation by not considering the formation of cross linkages (i. e., three-dimensional polymerization). Therefore it was necessary to carry out experiments to obtain the data of Table I which shows the effect on the end product by attempting to resinify (*a*) by heating solutions of monomethylolurea, dimethylolurea, and a mixture of equal parts of each, and (*b*) by varying the molecular ratios of the urea and formaldehyde in aqueous solutions.

TABLE I. TESTS FOR RESINIFICATION OF DIMETHYLOLUREA, MONOMETHYLOLUREA, AND THEIR PARENT SUBSTANCES AT 100° C.

pH of Solution	Acid, 4–7	Neutral, 7	Basic, 7–9
Case I:			
A. 1 mole monomethylolurea[a]	WP[b]	WP	WP
B. 1 mole urea + 1 mole formaldehyde	WP	WP	WP
Case II:			
A. 1 mole dimethylolurea[a]	Gel	Gel	Gel
B. 1 mole urea + 2 moles formaldehyde	Gel	Gel	Gel
Case III:			
A. 1 mole monomethylolurea[a] + 1 mole dimethylolurea	Gel	Gel	Gel
B. 1 mole urea + 1.5 moles formaldehyde	Gel	Gel	Gel

[a] To the dry powders, an equal weight of distilled water was added.
[b] White powder.

PREPARATION OF DIMETHYLOLUREA. The dimethylolurea was prepared by causing 1 mole (60 grams) of urea to react with 2.1 moles (170.27 grams of 37 per cent CH_2O) of aqueous formaldehyde for 15 hours at 18–25° C. at pH of 7–8, obtained by adding sodium hydroxide and buffering with monosodium phosphate. The dense white precipitate which formed was filtered from the supernatant liquid, washed reasonably dry with anhydrous alcohol, and vacuum-dried. Nitrogen: calculated, 23.33 per cent; found, 24.05 per cent.

PREPARATION OF MONOMETHYLOLUREA. The monomethylolurea was prepared by reacting 1 mole (60 grams) of urea with 1 mole (81 grams of 37 per cent CH_2O) of aqueous formaldehyde at a pH of 7–8, obtained by the addition of barium hydroxide at room temperature (25° C.), and precipitating the barium as carbonate when the formaldehyde content became substantially zero. Nitrogen: calculated, 30.11 per cent; found, 29.20 per cent.

In view of the great difficulty of preparing pure monomethylolurea, the possibility of some contamination should not be overlooked, but probably any contamination with the presence of dimethylolurea or any other substance would tend to promote reactivity and formation of cross linkages rather than to hinder them.

In cases I*A*, II*A*, and III*A* the materials were heated at approximately 100° C. in open beakers for 2 hours unless gelation occurred previously. In cases I*B*, II*B*, and III*B* the reactions were carried out at 100° C. simultaneously with cases I*A*, II*A*, and III*A* but in the apparatus described above.

When the aqueous monomethylolurea suspension of case I*A* was heated, no evidence of gel formation was observed. The white powder, obtained upon evaporation of the water in the monomethylolurea suspension, differs radically in properties from the condensate formed from the similar treatment of dimethylolurea which resulted in gel formation.

In case I*B* the white powder, obtained by reaction of 1 mole of urea and 1 mole of formaldehyde, appeared to be identical with that formed in case I*A*—i. e., no gelation.

In cases II*A*, II*B*, III*A*, and III*B* there was no doubt that irreversible gel formation rapidly took place because of the easy physical observation of the phenomena—i. e., the formation of a continuous hard, white, glasslike gel structure which did not remelt upon heating and which did not dissolve in solvents such as acetone and toluene.

In order to make the evidence more conclusive, an attempt was made to dissolve the monomethylolurea in order to have an opportunity to advance or polymerize the monomethylolurea while it was in a homogeneous system—i. e., in solution—rather than to try to react it in a heterogeneous system consisting of a suspension of the white powder in aqueous medium. The monomethylolurea was found to be only partially soluble in water, in methanol, in acetone, in methyl isobutyl ketone, or in ammonium hydroxide. A reference to Einhorn and Hamberger (*7*) for true solvents for monomethylolurea showed that none were known. Both monomethylolurea and dimethylolurea were found to be completely soluble in concentrated hydrochloric acid.

A solution of monomethylolurea in concentrated hydrochloric acid was heated at the boiling point until it evaporated to dryness. A residue which looked like a resin while still warm was found to crystallize on cooling. These crystals dissolved in concentrated hydrochloric acid. On the other hand, a solution of dimethylolurea in concentrated hydrochloric acid was also evaporated to dryness in a similar way, but this advanced as usual to a transparent, water-white gel in a very convincing manner.

All these experiments showed that dimethylolurea or mixtures of monomethylolurea with dimethylolurea form gels readily without question. On the other hand, the experiments with monomethylolurea showed no gel formation whatever. It is true that when the heating was vigorous enough to produce a partial charring with the odor of decomposing urea, accompanied by the smell of ammonia and confirmed by turning litmus blue, a final dark gummy residue was obtained as a partially charred mass. This, however, cannot be interpreted as proof of true gelation of monomethylolurea when it is remembered that a multitude of organic compounds will decompose to a tarry mass resembling a gel if heated to destruction. If, however, in a solution in which the solvent was also the most active catalyst known (i. e., low pH), monomethylolurea did not form a gel and dimethylolurea, under the same conditions, did form a gel, it does not appear likely that monomethylolurea will form a gel under any circumstances without the addition of some other substance capable of forming cross linkages (e. g., some dimethylolurea).

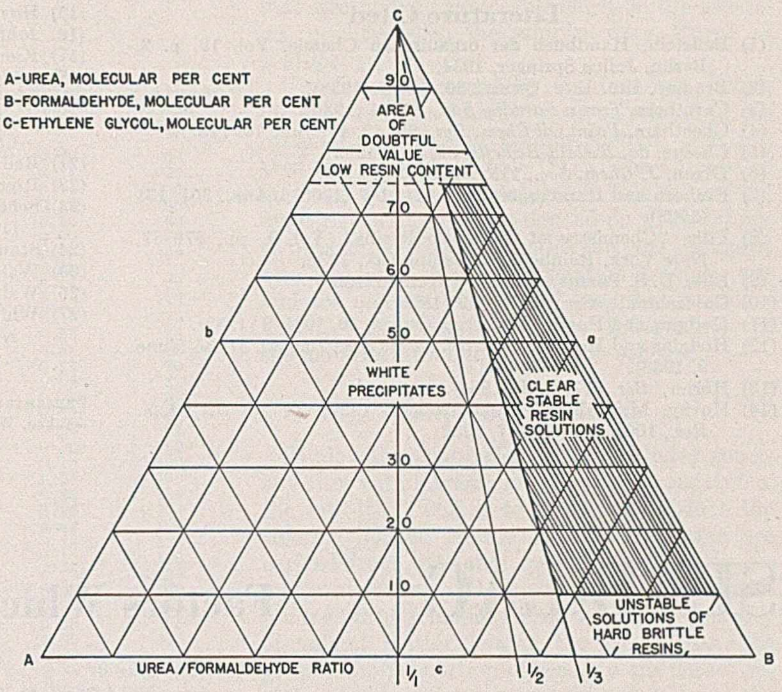


FIGURE 1. TRIAXIAL DIAGRAM OF UREA–FORMALDEHYDE–ETHYLENE GLYCOL SYSTEM

Stability of Urea–Formaldehyde–Ethylene Glycol Condensation Products

The formaldehyde, ethylene glycol, and ammonia were carefully weighed and placed in the flask of the apparatus described and agitated for fully 5 minutes before the urea was added. Heat was applied to the bath. Approximately 15 minutes were required to bring the system to boiling. The resin was refluxed for 60 minutes at 87–88° C. The resins were then cooled to room temperature, weighed, adjusted to 40.0 per cent resin content with distilled water, and stored for stability tests. The resin content of the urea–formaldehyde–ethylene glycol system was determined by heating a 1.0–1.5 gram sample in the oven at $103 \pm 1°$ C. for 1.5 ± 0.1 hours. If the solid content was greater than 40 per cent, distilled water was added in order to bring all the samples to this concentration of solids as determined by the above method.

TABLE II. STABILITY OF AQUEOUS 40 PER CENT SOLUTIONS OF UREA–FORMALDEHYDE–ETHYLENE GLYCOL RESIN COMPOSITIONS AT ROOM TEMPERATURE

Expt. No.	Composition, Moles: Moles	Formaldehyde	Ethylene glycol	NH_4OH	Initial Gardner-Holdt Viscosity (25° C.)	Stability[a]: 2 weeks	4 months	6 months	Final Gardner-Holdt Viscosity (25° C.)
1	1	1	0	0.04	A	WP	...	...	..
2	1	1	1.0	0.04	A	WP	...	...	..
3	1	2	0	0.04	A	WP	...	...	..
4	1	2	0.33	0.04	A	WP	...	...	..
5	1	2	0.67	0.04	A	WP	...	...	..
6	1	3	0	0.04	A	OK	WP	...	..
7	1	3	0.40	0.04	A	OK	WP	...	..
8	1	3	1.0	0.04	A	OK	OK	OK	A
9	1	3	2.0	0.04	A	OK	OK	OK	A
10	1	3	3.0	0.04	A	OK	OK	OK	A
11	1	3	4.0	0.04	A	OK	OK	OK	A
12	1	3	5.0	0.04	A	OK	OK	OK	A
13	1	4	0	0.04	A	OK	WP	...	..
14	1	4	1.26	0.04	A	OK	OK	OK	A
15	1	5	1.0	0.04	A	OK	OK	OK	A

[a] WP = resin becomes a solid white precipitate.

Table II shows the results of several significant runs.

When the data from Table II are plotted on a triaxial diagram (Figure 1), there are areas of composition which determine the stability of the resulting resin solution.

Stability was determined by storage of the resin solution in glass bottles, equipped with a metal screw top with cork gaskets to ensure against loss of volatile matter. These bottles were set in a closed box inside a dark cabinet to prevent any photocatalytic changes. The formation of white precipitates, even in a premature way—i. e., by development of opacity or cloudiness in solution—was considered sufficient instability for concluding tests. An increase in viscosity would also be evidence of another type of instability, but Table II shows that the viscosity of these resin solutions did not increase appreciably—i. e., not within the limits of the measuring device employed.

From other experiments it appears that this area of stability as shown in Figure 1 is specific to ethylene glycol, and that when other polyhydric alcohols are employed to replace ethylene glycol, the areas are not necessarily congruent.

Discussion

Although these so-called water-soluble urea-formaldehyde resins are soluble in water in the initial stages, they are converted by heat to the irreversible gel state.

The formation of gels does not take place from pure monomethylolurea or from 1 mole of urea and 1 mole of formaldehyde; nevertheless, gelation does take place quite readily if the molecular ratio of formaldehyde to urea exceeds 1 to 1, because the presence of even a slight amount of dimethylolurea greatly augments the formation of gels by forming three-dimensional structures through the development of cross linkages.

From the structural concepts given in the early part of the paper, it will be seen that when the molecular ratio of formaldehyde to urea is equal to or greater than 2 to 1 (where the reacting material is thus all dimethylolurea), the tendency to form the structure shown under case II is very great. This structure, which has the greatest chance of being formed, is the same as the structure which was assumed by Dixon (*6*), Cheetham (*4*), Pearce (*20*), and many other investigators and which led to the recognition of the unit polymer.

Acknowledgment

The writers wish to thank Reichhold Chemicals, Inc., for permission to publish this article and Herbert Hönel of Beckacite Kunstharzfabrik, G. m. b. H., for kind suggestions and criticism.

Literature Cited

(1) Beilstein, Handbuch der organischen Chemie, Vol. 19, p. 2, Berlin, Julius Springer, 1934.
(2) Bradley, Ind. Eng. Chem., 30, 690–1 (1938).
(3) Carothers, *Trans. Faraday Soc.*, 32, 44 (1936).
(4) Cheetham, *Paint Oil Chem. Rev.*, 99, 42, 44 (June 10, 1937).
(5) Chesne, de, *Kolloid-Beihefte*, 36, 387 (1932).
(6) Dixon, *J. Chem. Soc.*, 113, 238 (1918).
(7) Einhorn and Hamberger, *Ber.*, 41, 24–7 (1908); *Ann.*, 361, 131 (1908).
(8) Ellis, "Chemistry of Synthetic Resins", Vol. I, pp. 576–87, New York, Reinhold Publishing Co., 1935.
(9) Ellis, U. S. Patent 2,115,550 (April 26, 1938).
(10) Goldschmidt, *Ber.*, 29, 24–39 (1896).
(11) Hodgins and Hovey, Ind. Eng. Chem., 30, 1021–9 (1938).
(12) Hodgins and Hovey, *Paint Oil Chem. Rev.*, 100, 30, 31, 35 (June 9, 1938).
(13) Hölzer, *Ber.*, 17, 659 (1884).
(14) Hovey, M.S. thesis, Union College, 1927; *Paint Oil Chem. Rev.*, 100, 5–11 (July 7, 1938).
(15) Hovey and Hodgins, U. S. Patent 2,109,291 (Feb. 22, 1928).
(16) John, U. S. Patent 1,355,834 (Oct. 19, 1920).
(17) Kienle, Ind. Eng. Chem., 22, 590–4 (1930).
(18) Lüdy, *Monatsh.*, 10, 205 (1889).
(19) MacDonough, U. S. Patent 2,034,479 (March 17, 1936).
(20) Pearce, *Official Digest Federation Paint & Varnish Production Clubs*, 8, No. 167, 216–20 (1937).
(21) Redfarn, *Brit. Plastics*, 5, 238 (1933).
(22) Ripper, U. S. Patent 1,687,312 (Oct. 9, 1928).
(23) Scheibler, Trostler, and Shulz, *Z. angew. Chem.*, 41, 1305 (1928).
(24) Staudinger, *Ber.*, 59, 3019 (1926).
(25) Walter and Lutwak, *Kolloid-Beihefte*, 40, 158 (1934).
(26) Walter and Oesterreich, *Ibid.*, 34, 115 (1931).
(27) Whitmore, "Organic Chemistry", p. 225, New York, D. Van Nostrand Co., 1937.

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SEED-LAC

Factors Which Affect Bleaching Quality

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Kusum and khair lacs apparently produce the best grades of seed-lac for bleaching; the ber and palas hosts yield products which are, in general, inferior in this respect. The quantity of sodium hypochlorite consumed in producing a bleached lac of a standard color depends primarily on the amount of nitrogenous material which is soluble in soda, and to a lesser extent in most cases on the color of the seed-lac. The effect of age of the lac was apparent only when seed-lacs of the same origin were compared for the length of time they were stored as seed-lac. Storing stick-lac under conditions which tend to block it affects the bleaching quality adversely. The total amount of material which was soluble in boiling alcohol or acetone was not of consequence.

The large use of seed-lac for the manufacture of "white shellac" has made the bleaching quality an important property in the sale of this commodity. The explanation of why some seed-lacs consume more bleach solution than others in being converted to a standard color is therefore a subject of particular interest, especially to dealers in seed-lac, who are now frequently called upon to supply this material on a basis of bleachability. The bleach consumed would be proportional to the quantity of coloring matter present, if this were the only material in lac which reacted with the bleaching solution. It has been found, however, that other impurities associated with seed-lac as well as the resinous constituents of lac also consume a bleach solution. The nitrogenous matter derived from the body of the lac insect is one of these impurities (*4, 6*).

The age of the seed-lac and the amount of insolubles present may also have an effect. This paper reports a study of the nature and extent of the influence of these and other factors on the amount of bleach consumed.

Bleach Solution Consumed

Stick-lacs of known origin were converted to seed-lac after having been stored under standard conditions for different periods in the experimental lac factory at the Indian Lac Research Institute, Namkum. The bleaching qualities of the resulting seed-lacs were then determined.

The bleaching test employed was as follows:

Thirty-gram samples of seed-lac (ground to 30 mesh) were dissolved in 200 cc. of an aqueous solution containing 3 grams of sodium carbonate at 70–75° C. This procedure required 2.5 hours. The solution was then cooled to room temperature, and the volume made up to 300 cc. with water. This solution was passed through a 100-mesh sieve, and 250 cc. of the filtrate were taken for bleaching. The bleach was carried out at 35° C. by the addition of 20 cc. of a sodium hypochlorite solution containing 3 per cent available chlorine. When the lac solutions had consumed all of the free chlorine, as indicated by starch-iodide paper, the bleach solution was further added in 2–5 cc. portions until they matched as nearly as possible the color of a slightly underbleached solution of kusum seed-lac. A fair idea was obtained under these circumstances of the relative bleachability of the different seed-lacs in terms of cubic centimeters of the bleaching solution. Thus, the bleaching values given in the tables refer to cc. of the bleaching solution (3 per cent available chlorine) required for thirty grams of seed-lac.

The results are arranged in Table I in the order of increasing bleaching value. The amount of bleach required increased, in general, with the increase in nitrogen content of the sample. The few exceptions are marked (*b*) in Table I.

A closer agreement was obtained when the bleaching values were compared with the nitrogen content of aqueous extracts of these seed-lacs, such as is shown in Table II for eight typical samples of the series shown in Table I. The bleach solution consumed corresponded approximately to the nitrogen con-

Table I. Properties of Seed-Lacs

Sample No.	Variety[a]	Age as Stick-Lac	Age as Seed-Lac	Color Index	Nitrogen Content	Bleaching Value
		Months	*Months*		%	*Cc.*
C308	K × Kh, Ag, Ph	0	1	7.0	0.09	50
C59	K × K, Ag, Ph	0	40	9.2	0.11	59
C49	K × Br, Ag	0	40	10.0	0.11	59
C48	K × Kh, Ag, Ph	0	40	10.2	0.12	60
C153	K × Kh, Ag, Ph	12	28	8.6	0.16	60
C254	K × Kh, Ag	0	16	8.8	0.09	62
C307	K × K, J, A	0	0	11.4	0.20	69
C301	Ber × Ber, B ,A	1	2	11.0	0.20	70
C256	K × Kh, Ag, imperfect wash	0	16	11.0	0.14	73
C154	K × Ber, Ag	12	28	13.0	0.15	73
S121	K × K, Ag, A	37	0	13.5	0.16	73
C255	P × P, Kt, A	31	16	14.6	0.26	75
C226	P × P, Kt, A	27	20	13.2	0.28	77
S100	K × K, J, Ph	43	0	15.7[b]	0.28	79
C298	P × P, B, A	0	2	10.8	0.24	82
C297	Ber × Ber, B, A	0	2	11.6	0.25	82
C257	P × P, Kt, A, imperfect wash	31	16	14.0[b]	0.32[b]	87
C251	P × P, B, A	12	28	11.8	0.29	87
S153	K × K, J, A	32	0	14.0[b]	0.36[b]	92
C252	Mixed lac, Kt	4	16	11.0	0.16	100
C253	Ber × Ber, B	8	11	12.0	0.27	100
C303	P × P, B, A	1	1	13.8	0.29	104
C315	Mixed lac, B	? + 2	14	15.4	0.26	104
S12	K × K, J, Ph	56	0	16.5	0.43	109
C310	Ber × Ber, B, immature crop	0	0	15.6	0.48	110
C158	BrK, Ph	?	28	40.0	0.19[b]	120
C157	BrK, A	?	28	46.0	0.27[b]	125
S256	BrK, A, blocked	6	0	31.0[b]	0.41	130
S257	BrK, Ph, blocked	5	0	26.0[b]	0.28[b]	135
C228	P × P, Kt	28	20	16.0[b]	0.65	155
C225	P × P, B, A	46	20	19.8[b]	1.00	155

[a] K = kusum, Kh = khair, P = palas, Ph = phunki, A = ari, B = Baisakhi crop, Kt = Katki crop, J = Jethwi crop, Ag = Aghun crop or kusmi, Br = Burma kusum; K × Kh, etc., used to denote crossed varieties where previous generation of insects were raised on a different host than the one designated by the second symbol; i. e. K × Kh = previous generation upon kusum trees while present generation is producing lac upon khair trees.

[b] Exceptions to general tread of experiments.

tent of the extract with the exception of the three samples marked (*a*). Two of these samples were kusum lacs from Burma and the third was commercial Katki seed-lac which had probably been blended with Burma kusum lac. Table I shows that these samples had an abnormally high color index, which is another factor affecting the bleachability of the seed-lacs. Samples C153 and C252 are interesting to compare in this respect. Both contained the same amount of total nitrogen, but the latter gave an extract which contained nearly four times as much nitrogen as that from the former lac.

Table II. Effect of Soluble Nitrogenous Impurities

Sample No.	N Content in 300 Cc. of Extract	N in Original Seed-Lac	Bleach Required for 300 Cc. of Extract
	Cc. 0.1 N NaOH	%	*Cc.*
C153	4.2	0.16	59
C158[a]	13.2	0.19	115
C252[a]	15.6	0.16	104
C157[a]	27.6	0.27	134
C257	30.0	0.32	90
C310	40.8	0.48	120
C225	53.4	1.00	153
C228	55.2	0.65	153

[a] Bleach solution consumed did not correspond to the nitrogen content of the extract.

Effect of Age and Insolubles on Bleaching

The age of the sample and the amount of the insolubles have also been generally considered important. This was not wholly substantiated in the present investigation, as Table III shows. The effect of age is apparent only when seed-lacs of the same variety and host origin are compared for the length of time they were stored as stick-lac. This is clearly demonstrated in Table IV. The dye and the protein matter apparently suffered a change during the aging as stick-lac, so that they were imperfectly washed by water during the preparation of the seed-lac. Table I shows clearly that age had no noticeable effect on the bleaching quality when the samples were stored as seed-lac.

The claim advanced by Gardner and Harris (*1*) that the bleachability may be related to the material insoluble in boiling acetone does not hold for seed-lacs (Table III). The amount of material which was insoluble in this solvent (*2*) appeared to more or less depend on the total age of the sample (the age as stick-lac plus the age as seed-lac), but there is no relation between age and the amount of material insoluble in boiling alcohol. Bleachability is also independent of the material insoluble in the latter solvent.

Influence of Variety

Table I shows also that the color index generally rises with increase in the nitrogen content of the seed-lac. This is to be expected, since the coloring matter, laccaic acid, and nitrogen are derived from the same source—namely, the remains of insects. Hence, the chief factor determining the bleachability of seed-lac is the quantity of animal matter left in the lac. Thus, the greater the proportion of resin to the insect remains in the stick-lac, the better will be the bleachability of the seed-lac prepared from it. Table I shows that the best bleaching grades were kusum and khair seed-lacs. Next in order were the varieties crossed with kusum. (See note, Table I.) Ber and palas gave the poorer bleaching grades. This was the same order as the amount of resin secreted by the insect upon different hosts (*6*).

Table III. Effect of Insoluble Material

Sample No.	Total Age	Hot Acetone Insolubles	Hot Alcohol Insolubles	Bleaching Value
	Months	%	%	*Cc.*
C307	0	...	3.18	69
C310	0	...	7.12	110
C308	1	16.59	1.36	50
C298	2	4.3	4.29	82
C297	2	4.56	4.48	82
C303	2	4.96	4.66	104
C301	3	3.68	3.75	70
C254	16	4.41	1.50	62
C256	16	4.60	4.96	73
C253	19	6.84	4.13	100
C252	20	7.55	3.56	100
C59	40	13.25	2.27	59
C49	40	12.39	1.63	59
C48	40	10.54	1.85	60
C315	? + 16	14.86	7.93	104
C154	40	15.11	2.59	73
C153	40	8.60	1.07	60
C255	47	15.99	5.32	75
C226	47	16.76	3.62	77
C257	47	16.01	4.62	87
C225	66	18.64	12.69	155

Table IV. Effect of Age

Sample No.	Variety	Age as Stick-Lac	Age as Seed-Lac	Nitrogen Content	Color Index	Bleaching Value
		Months		%		*Cc.*
C49	K × Br	0	40	0.11	9.2	59
C154		12	28	0.15	13.0	73
C225	P, B, A	31	16	0.26	14.6	75
C226		27	20	0.28	13.2	77
C307	Kusum, A, Kt	0	0	0.20	11.4	69
C153		32	0	0.36	14.0	92
C59	Kusum, Ph	0	40	0.11	9.2	59
S100		43	0	0.28	15.7	77
S12		56	0	0.43	15.6	110

The proportion of insect remains is increased if the crop is highly parasitized, if it is immature, or if the stick-lac has been imperfectly washed. Storage of stick-lac under blocky conditions of heat and pressure also contributes to the imperfect removal of these impurities during washing. All such samples had comparatively poor bleaching characteristics, as Table V shows. Thakur demonstrated in his study of stick-lac (*5*) that efficient washing reduces the nitrogen content of the seed-lac and thus causes a corresponding improvement in the bleachability of the lac. He prepared in this manner a ber seed-lac having the bleaching characteristics of the kusum lac.

TABLE V. EFFECT OF POOR PREPARATION

Sample No.	Variety and Treatment	Age as Stick-Lac	Hot Alcohol Insolubles	Color Index	N Content	Bleaching Value
		Months	%		%	*Cc.*
1	K × Kh, well washed	0	1.5	8.8	0.09	62
2	Same as 1 but imperfectly washed	0	5.0	11.0	0.14	73
3	Palas, well washed	31	5.3	14.6	0.26	75
4	Same as 3 but imperfectly washed	31	4.6	14.0	0.32	86
5	Ber, immature crop	0	7.1	15.6	0.48	108
6	Khair, stick-lac stored under block conditions	..	...	..	0.27	72
7	Same as 6, stored well	..	...	..	0.20	62

Influence of Fineness of Grinding

Among other factors which influence the amount of bleach solution consumed were those encountered in the process of bleaching itself. One of these factors was the fineness to which the lac had been ground before it was dissolved. The effect of grinding is illustrated in Table VI, which clearly shows that coarsely ground samples required considerably less bleach than the finely ground ones. This difference was even more apparent in the poor bleaching grades than in good grades of seed-lac. For the last two samples in Table VI, the soda solutions of seed-lac were filtered through filter paper, and the insolubles remaining on the filter paper were washed, dried, and weighed. It appears from the amounts of insolubles found in these two instances that in the crushed state more of the insect remains passed through the 100-mesh sieve to increase the bleach consumption than was the case when the samples were not ground.

TABLE VI. EFFECT OF GRINDING

Sample No.	Cc. of Bleach Required	
	Unground	Ground to 40 Mesh
C226	94	100
C228	108	142
C257	81	89
C59	54	56
C225	112	120
Soda insolubles, %	13.5	8.5
C255	64	66
Soda insolubles, %	8.3	5.2

Alkalinity of Dissolving and Bleaching Medium

The concentration of the soda solution, the time, and the temperature employed in dissolving the lac also influenced the consumption of the bleaching liquor. The effect of the concentration of soda solution upon the quantity of bleach consumed has already been studied (*3*) in the case of shellac. Table VII illustrates the effect of varying the duration and temperature of this operation.

The consumption of bleach was increased by high temperatures and longer periods used in dissolving the lac. This effect was more marked with concentrated soda solutions. It was also greater with seed-lacs than with shellacs. This was due unquestionably to a greater proportion of the nitrogenous matter which dissolved in the former instances.

Not only the alkalinity of the dissolving medium but also the alkalinity of the bleaching liquor affected the consumption of bleach. In the equation $NaOCl + H_2O \rightleftharpoons NaOH + HOCl$ the equilibrium was displaced to the right as hypochlorous acid was consumed by the lac. Thus, the alkali concentration was increased during the bleaching reaction. In the bleaching of poor quality seed-lacs, therefore, the alkalinity may become very high on account of the greater amount of bleach used. This high alkalinity had two adverse effects. It tended to reduce the availability of the bleaching agent by displacing the equilibrium to the left and to hydrolyze the complex proteoses and peptones. These proteoses were extracted by the soda solution from the insect remains; when hydrolyzed, they formed simpler peptides and amino acids, which reacted with more bleach than the complex nitrogenous matter originally present in the lac. There was also a tendency for the bleached lac to lose some of its chemically combined chlorine and to regain its color under these conditions. This would account for the fact that the poorest quality seed-lacs could not be bleached to the same lightness of color as the others, regardless of the quantity of bleach added. The following example clearly illustrates the effect of alkalinity: Thirty grams of a sample of Burma kusum seed-lac required 145 cc. of a bleaching solution of 3 per cent available chlorine of alkalinity 0.77 *N*. When a bleaching solution of alkalinity 0.47 *N* was employed, only 115 cc. of the bleach solution were required. Thus, bleaching solutions of high alkalinity enhance the bleaching value and exaggerate the differences that exist between different seed-lacs.

TABLE VII. EFFECT OF VARIATIONS IN METHOD OF DISSOLVING LAC

Sample No.	Na_2CO_3	Temp.	Time	Bleaching Value
	%	° *C.*	*Min.*	*Cc.*
F428	2.0	60	60	57
		80	150	75
		80	240	90
		85	300	105
F364	1.0	60	60	45
		90	180	57

Acknowledgment

This article describes part of an investigation which was undertaken as a joint research project by the Indian Lac Research Institute and the Shellac Research Bureau of the Polytechnic Institute of Brooklyn. It was sponsored by the Indian Lac Cess Committee and the United States Shellac Importers Association. This paper is a contribution of the Indian Lac Research Institute and of the Shellac Research Bureau. The article for the most part is based on the investigations of N. N. Murty. Data for the material insoluble in boiling acetone and boiling alcohol were obtained at the Polytechnic Institute of Brooklyn. The authors wish to thank Dr. Sen for helpful suggestions in writing the paper, and to Mr. De for assistance given in determining color index.

Literature Cited

(1) Gardner, W. H., and Harris, H. J., Ind. Eng. Chem., Anal. Ed., 6, 400 (1934).
(2) Gardner, W. H., Koprowski, L., and Murty, N. N., Ind. Eng. Chem., to be published.
(3) Murty, N. N., *J. Univ. Bombay*, 2, Pt. 2, 301–6 (1933).
(4) Murty, N. N., and Aldis, R. W., Indian Lac Research Inst., *Research Note* 15 (1934).
(5) Thakur, A. K., *Ibid.*, *Bull.* 27 (1937).
(6) Venugopalan, M., *Ibid.*, *Bull.* 11 (1932).

AIR CONDITIONING

Nonregenerative "Calorider" Performance

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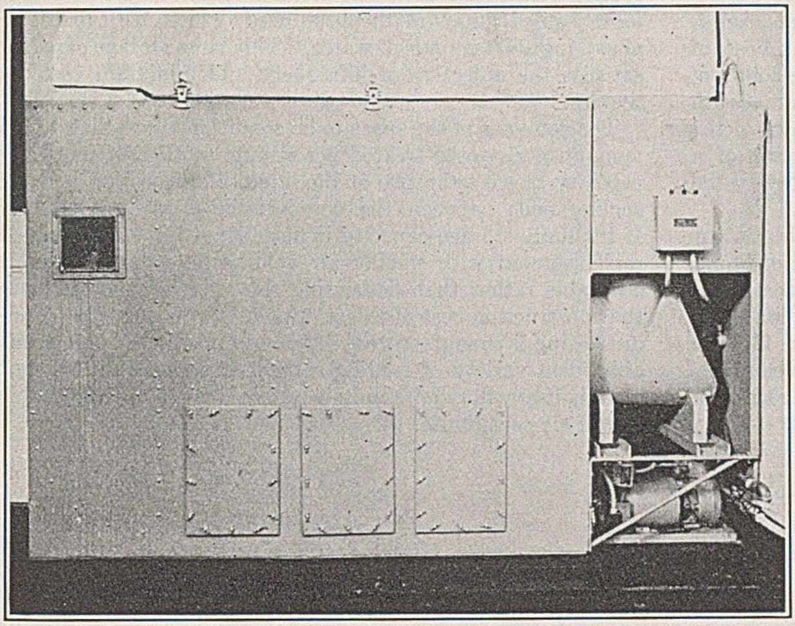

FIGURE 1. FRONT VIEW OF "CALORIDER"

THE preceding paper (*1*) gave special attention to residential air-conditioning requirements. Illustrations were shown of an early form of apparatus used for dehumidifying and cooling air in summer and humidifying and heating air in winter to illustrate the principles of the method.

This paper deals with an improved form of apparatus and summarizes the results obtained with various test installations. Figure 1 shows the front of this type of apparatus suitable for treating up to 1500 cubic feet of air per minute in which the resistance at maximum air flow is less than 2.25 inches of water pressure. The air enters by a duct attached to the top of the "Calorider" at the left end, is drawn through the liquid- and solid-phase sections of the unit by the blower at the right, and is discharged to a duct through the wind box above the blower. The moisture absorbing material, "Caloride", is charged into the top of the unit through a hinged lid. "Caloride" is a specially prepared hydrated calcium chloride in molded lump form containing about 72 per cent calcium chloride and normally only a small proportion of activated carbon for removing odors. Three small doors shown at the front of the compartments may be used if it is desired to remove the unused "Caloride" at the end of the period requiring dehumidification of air. Such a unit is 83 inches long, 53 inches high, and 28 inches wide. It may be moved into its operating location through any ordinary door or passageway on skids or rollers by two men. The length can be reduced to 64 inches for handling in unusually restricted quarters by removing the blower and wind box. Within these small over-all dimensions the novel principles of this design provide for the treatment of air volumes which are sufficiently large for the great majority of houses or spaces of similar character.

The principal operating cost factor is the delivered cost of "Caloride." The production cost of "Caloride" is low as compared to the delivered cost to the residence. The difference is due principally to the freight, package, and local delivery charges.

The cost of freight per ton of "Caloride" in carload lots from factory to warehouses in the average areas of consumption is the least important of these three items.

The package cost per ton depends upon the size of the individual package and this will be governed by the strength of the person who has to lift it 4.5 feet to the top of the apparatus. Truckmen can do this with a 100-pound bag. Householders cannot be expected to handle a package heavier than 60 pounds even if they are willing to exert themselves to that extent, and only a small proportion employ "hired men." Smaller containers place a prohibitory burden on the operating cost of household air conditioners of this type. The package should therefore be as large as possible, preferably containing 100 pounds of material in order to minimize its effect upon the cost of "Caloride."

The quantity delivered per trip is still more important than the package size from the cost standpoint. In the majority of cases this quantity will be dictated by the storage capacity of the "Calorider" itself, which is limited by its permissible dimensions.

Therefore storage capacity within the apparatus must be as large as possible, and this has been attained by reducing the volume of other apparatus parts to a minimum. The structure of the apparatus is shown in Figure 2.

These parts other than storage bins are the blower, the cooling coils between the lump compartments, and the liquid-phase air-pretreating section. If desired, the blower can be a separate unit and placed at any point in the duct system. The cooling coils and lump compartments occupy little space. The small size of the liquid-phase section in this unit as compared to that shown in the first paper of this

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series (*1*) is the result of extensive experimental work and will be discussed here in some detail.

Improved Form of "Calorider"

Early work had shown that the velocity of the air, while being dehumidified by contact with the "Caloride" lumps, could be very high and still give a close approach to the theoretical moisture removal. This presumed that the air had been pretreated by some means so that its moisture content upon entering the solid-phase section was low and relatively constant. A liquid-phase section was therefore required that could handle large volumes of inlet air with a variable moisture content and deliver an outlet air of constant humidity. In the earlier form of liquid-phase section, the air flowed countercurrent to the circulated solution over trays and through cascades at their ends, contacting first the diluted solution and last the most concentrated solution according to accepted engineering practice. The latent heat of condensation was converted to sensible heat in the solution, and this was removed by passing the solution in contact with a cooling coil immersed in a reservoir at the bottom of the apparatus. This necessitated the continual pumping of a large volume of solution to carry the generated heat to the cooling coil.

It was decided that if the heat were removed at the instant and place that it was formed, a much slower rate of liquid circulation would be adequate. An extended surface radiator was selected to attain this end in which the solution could be spread out on a very great area of fins in thin films in contact with the air, whereby the films could be cooled at the moment they absorbed moisture by a coolant flowing through the tubes.

The air-drying efficiency of such a liquid phase device was found to be surprisingly high which permitted the use of a very small compact air-predrying section. By this means most of the space within the prescribed over-all apparatus dimensions can be used for lump storage. A more detailed discussion of the advantages of concurrent flow absorption and countercurrent cooling will be presented in a later paper, but suffice it to point out here that it permits the passage of gases at high velocities with correspondingly high mass and heat transfer rates through closely spaced fin-tube radiators, whereas countercurrent flow causes flooding at much lower gas velocities.

In an apparatus 28 inches wide and 53 inches high, suitable for treating 1500 cubic feet of air per minute at low pressure, the liquid-phase section is 14 inches long and the solid-phase section 50 inches long. The latter section will hold a ton of loosely piled lumps of the type used, which are cabable of absorbing 1800 pounds of water. This large storage capacity satisfies the objective of infrequent and minimum cost deliveries.

The demands of the space to be conditioned will dictate the amount of air to be treated per minute so that with smaller capacity blowers the size of the liquid-phase section and the cooling coils between the compartments can be reduced. If the lump storage capacity is not changed, its frequency of replenishment with smaller air volumes is reduced; this is advisable rather than decreasing the storage capacity since the construction cost of this section is low. Hence, a standard casing is manufactured and is equipped with parts suitable for a variety of loading rates. Experience shows that most houses will require units treating from 500 to 1000 cubic feet of air per minute.

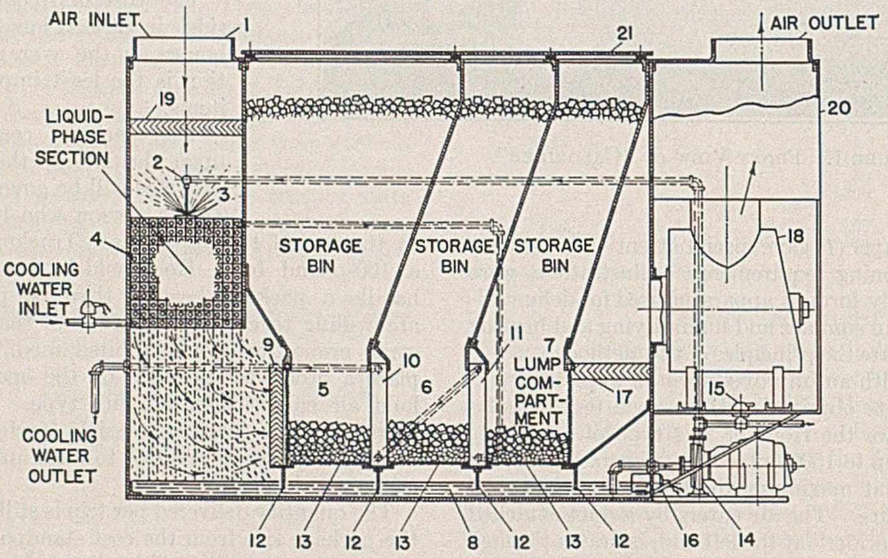


Figure 2. Vertical Section of "Calorider"

For convenient directional flow of the air, the radiator was set up so that the air and solution were premixed and entered at the top of the radiator, and were separated from each other at the bottom, and the solution was returned to the reservoir for mixing with the concentrated solution draining from the lumps. The air discharged horizontally through the bottom of the bed of lumps for further drying. By this means the air and solution flowed concurrently while the coolant—for example, water—passed countercurrent to both the air and the solution.

The raw air to be dried enters the apparatus (Figure 2) at 1 and is intimately mixed with the solution which is discharged from nozzles 2 and broken up by impingement targets 3. This method permits the use of nozzles with sufficiently large holes to prevent them from fouling. The solution absorbs moisture while in suspension in the air whereby its temperature is increased, and then passes concurrently with the air into finned-tube radiator 4. The solution spreads as thin films on the fins in contact with confluent, turbulent streams of air and is cooled. Further heat is generated in the films but is removed as formed, and the air and solution emerge from the bottom of the radiator substantially in moisture equilibrium with each other, regardless of the moisture content of the raw air. The solution returns to reservoir 8 and the air continues through spray eliminator 9, compartments 5, 6, and 7, and finned-tube cooling coils 10 and 11.

Baffles 12, whose bottom edges are sealed by the solution in the reservoir, prevent the air from by-passing the compartments and cooling coils. These baffles are restrained from conducting heat away from lump-supporting screens 13 by suitable placement or heat-insulating provisions; otherwise the screens may be cooled below the crystallizing temperature of the concentrated solution draining from the lumps.

Other features of the lump section are the same as those described in the preceding paper. The concentrated solution and the diluted solution draining from the liquid-phase section are mixed in the reservoir, and the mixture is sent back to nozzles 2 by pump 14. The discharge line from the pump is branched and contains a solenoid, 15, which is opened and closed by the rise and fall of the float in level controller 16 to discharge excess solution to the sewer or to a storage tank. Cooling water is passed through the radiators in series or in parallel as desired. In winter, heated water is passed through the radiators in place of the cooling water circuit used in summer, and if desired, solution or water may be sprayed into the air stream above or below radiator 4. Suitable float control means is provided for addition of make-up water to reservoir 8 as it is evaporated. A spray eliminator, 17, may be placed before blower 18. A backdrift spray eliminator may be used at 19. Sound-absorbing material may be used in wind box 20 or in the inlet section above eliminator 19. "Caloride" is charged to the storage bins through hinged lid 21.

Moisture Content and Relative Humidity

Tests made on the dehumidified air discharged from these units give useful results. Figure 3 shows how the moisture content and relative humidity of the discharge air varies with its temperature, regardless of the moisture content of the inlet air. The curve for grains of moisture per cubic foot of treated air is nearly a straight-line function of the temperature of the air up to about 74° F. Between this point and 87° F. the moisture content increases only from 2.75 to 3.0 grains per cubic foot; above 87° F. it again rises rapidly. The portion of the relative humidity curve within this range of 74° to 87° F. drops from 30.5 to 22 per cent, again indicating a fairly constant absolute humidity of the discharged air. Therefore, substantially the same quantity of moisture is removed by the "Caloride" whether the air is discharged at 74° or 87° F. This is an important factor when the temperature of the coolant, such as city water or cooling tower water, may vary or cannot be obtained at less than 80° to 82° F.; in the case of expensive water, its use can be conserved by operating in the higher ranges of this curve rather than in the lower. The result is essentially the same amount of dehumidification.

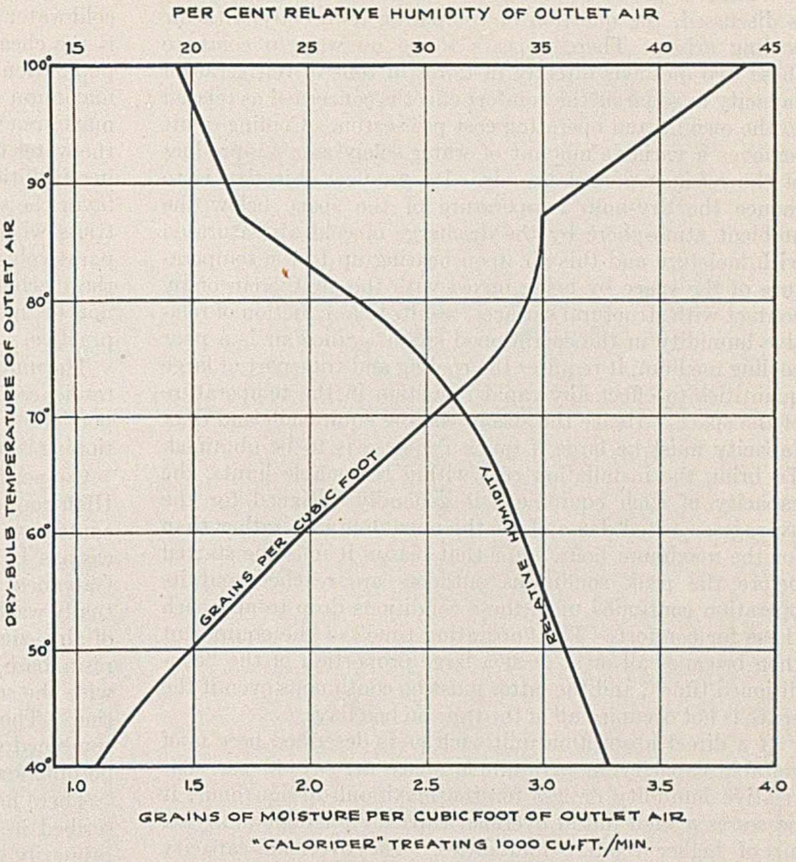


FIGURE 3. VARIATION OF MOISTURE CONTENT AND RELATIVE HUMIDITY WITH TEMPERATURE

Although the shape of this portion of the curve does not coincide with one of static equilibrium, it is analagous to the latter and is displaced only slightly to the right as a result of dynamic conditions. One explanation is that the film of calcium chloride solution is in contact with solid on one side but is absorbing moisture from the air on the other, and hence is unsaturated as to salt content. At other points the curve coincides with or parallels the vapor pressure curve of saturated solutions of calcium chloride.

The pretreatment of the air in the liquid-phase section eliminates the fluctuations of moisture content of the air supplied to the lump compartments, and the first compartment in the series receives air at about 40 per cent relative humidity. The lump compartments carry only the dehumidifying burden from this point down to the relative humidity of the outlet air, as Figure 3 shows.

When such a unit is treating 1000 cubic feet of air per minute, the contact time while passing through the three lump compartments is 0.3 second. Most of the moisture is taken out in the first compartment, and hence it is clear that the velocity of absorption is very high. This absorption velocity is, however, low compared to the liquid-phase pretreating section where heat removal is practically instantaneous at the point of its generation. In the pretreating section the contact time is about 0.1 second, but this section is capable of removing a much greater amount of moisture per unit time than can be removed by all three lump compartments.

Figure 2 shows that the storage bin above the first compartment is larger than either of the others. This is to compensate for the greater amount of "Caloride" consumed in the first compartment where most of the water is taken out by the solid-phase section.

Whenever air conditioning by direct moisture absorption is discussed, the question of comparing it directly with air cooling arises. There appears to be no way to compare these two methods directly in terms of tons of refrigeration capacity in so far as the comfort effect is concerned as related to the owning and operating cost per season. Cooling of air removes a variable amount of water solely as a by-product of the refrigeration of the air. Its primary objective is to reduce the dry-bulb temperature of the space below the ambient atmosphere by the discharge of cold air saturated with moisture and this air upon heating up to the temperature of the space by being mixed with the air therein or by contact with structural surfaces, results in a reduction of relative humidity in the conditioned space. Since air is a poor cooling medium, it requires the cooling and transport of large quantities to effect any rapid reduction in the temperature of the space. Hence the size of cooling equipment and duct capacity must be large if quick response is to be obtained. To bring the installation cost within reasonable limits, the capacity of such equipment is generally designed for the average expected demand for the maximum day rather than for the maximum hour. For that reason it must be started before the peak conditions outdoors are reached and its operation continued until these conditions drop to approach those for comfort. The "operating time" of the equipment then becomes all or at least a large proportion of the "conditioned time", and the latter must be continuous even if the space is not occupied all of the time on bad days.

If a direct absorption unit such as is described here is of suitable capacity to maintain a space at, say 40 per cent relative humidity or less for the maximum design hour, it possesses a high initial overload capacity for dehumidifying air of higher relative humidities. The overload capacity under such conditions is about 200 per cent of the normal operating capacity which, with a unit treating 1000 cubic feet per minute, is an absorption rate of as high as 50 pounds of water per hour. Even with high overloads, the relative humidity of the discharge air will correspond to the curve shown in Figure 3; this air passing into the space produces a noticeable cooling effect, due to evaporation of perspiration, after a very short time interval. It is not so dry or cold, however, that it is detrimental and consequently requires no extensive provision for distribution. The volume of air so treated need be only a fraction of that required as compared to the dry-bulb reduction method. This allows the use in existing houses of smaller ducts; in addition, since the dried air temperature is close to that of the building, the ducts need not be insulated to prevent the air from gaining heat from unconditioned spaces. The duct system is further simplified in that there is no stratification of cold air or of moisture in the conditioned space.

In addition to the creation of cooling effect by contact of the dry air with the summer-clothed body, there is also an initial, perhaps imponderable, dry-bulb temperature reduction of the space contents, depending upon the amount of moisture evaporated from furnishings such as textiles until they approach moisture equilibrium with the air.

Factors such as these make a direct comparison of the installation and operating costs of these two processes in terms of refrigeration impracticable. Experience with actual installations using absorption dehumidification appear to be the only suitable means of determining operating cost.

We do not claim that air should not be cooled for all purposes; this point should be emphasized. But dehumidification seems to be most suitable for the treatment of well-built residences and spaces of similar requirements. Experience with the test residence has shown this, and the same conclusion should apply equally well to residences in similar localities. Where dry-bulb reduction is required, cold water circulated through the radiators of the "Calorider" is the cheapest cooling means. There are 311 cities with a population of more than 20,000. Of these, about 155 have maximum water temperatures of 72° F., about 100 have a maximum water temperature of 65° F., and in about 60 cities the water temperature does not exceed 60° F. With increasing facilities for transportation, the tendency continues to favor the spreading of population to suburban and rural districts where wells of shallow depth can be driven at comparatively low cost. As in the case of the test residence, the discharged water can be used on the lawn and should not be more than is required for good lawn and garden practice.

The unit contains radiators of sufficient capacity to heat the residence in the winter by indirect warm air, and thus the portion of the equipment cost allocated to summer air conditioning is practically negligible.

Copper finned-tube radiators have been found satisfactory. High-copper-alloy piping, valves, pumps, etc., are used in contact with the solution. Red brass is satisfactory. The casings have been made of sixteen-gage galvanized iron or Galvaneal and their life is satisfactory when the parts actually washed by the solution are painted with a priming coat of zinc–zinc oxide paint and with a second coat of synthetic resin base paint. The galvanized surfaces not in contact with the solution, such as the bin walls, do not need protection. The materials used are of moderate price, and this, combined with the fact that close tolerances are not required, permits low-cost quantity production methods.

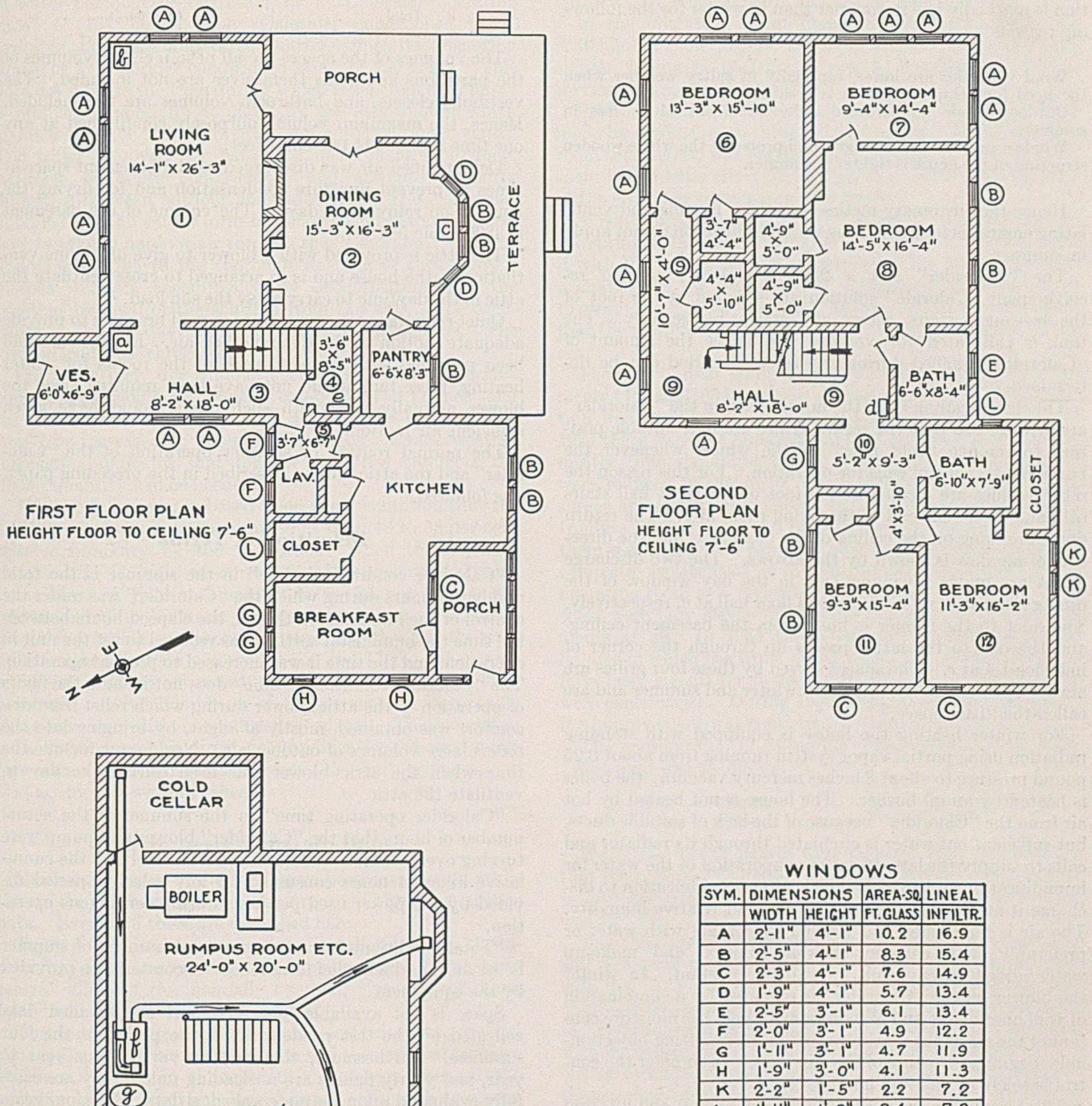
There has been no widespread use of units of the type described in this paper; the work so far has been concerned primarily with the testing of units under practical conditions for mechanical proficiency, the quality of the effect produced, and its cost.

Test Residence

This residence was conditioned during the summers of 1935, 1936, 1937, and 1938 by a "Calorider" and accurate records were kept of the use of water, power and "Caloride." Prior to this time an earlier form of the equipment was used during two summers for qualitative purposes. The residence is situated in a Connecticut town within commuting distance of New York, about 1000 feet from the shore of Long Island Sound and faces north-northeast.

It is a wood frame house of good construction with a black slate roof comprising a main portion and a setback wing as shown in Figure 4. A third floor (not shown) contains two rooms and bath. The windows are single-pane double-hung wood sash without weather stripping. The table on Figure 4 shows the area of the individual windows in square feet and the lineal feet for calculating infiltration when closed. The table also gives the dimensions of the outside doors. The total number of windows is fifty-five but nineteen of them are in portions of the house that have not been conditioned in past summers—ten in the kitchen wing and nine on the third floor. The third floor was not conditioned by the "Calorider." The kitchen is separated by self-closing doors from the rest of the house. Half-inch Celotex insulating board is nailed to the lower edge of the roof rafters of approximately half the roof area. No rock wool or other insulation is present in the exterior walls of the house but a small area of sloping ceiling of bedroom 12 is filled between the rafters with rock wool. No awnings are used on the windows.

This information is typical of that normally required by air-conditioning engineers to calculate the size of equipment and installation and operating costs using conventional re-



WINDOWS

SYM.	DIMENSIONS		AREA-SQ.	LINEAL
	WIDTH	HEIGHT	FT. GLASS	INFILTR.
A	2'-11"	4'-1"	10.2	16.9
B	2'-5"	4'-1"	8.3	15.4
C	2'-3"	4'-1"	7.6	14.9
D	1'-9"	4'-1"	5.7	13.4
E	2'-5"	3'-1"	6.1	13.4
F	2'-0"	3'-1"	4.9	12.2
G	1'-11"	3'-1"	4.7	11.9
H	1'-9"	3'-0"	4.1	11.3
K	2'-2"	1'-5"	2.2	7.2
L	1'-11"	1'-8"	2.4	7.2

DOORS

LOCATION	WIDTH	HEIGHT
KITCHEN	2'-6"	6'-8"
DINING ROOM	4'-0"	6'-8"
LIVING ROOM	4'-0"	6'-8"
FRONT	3'-0"	6'-8"

FIGURE 4. FLOOR PLANS OF AIR-CONDITIONED HOUSE

frigeration methods. Such refrigeration equipment, however, has only a summertime function.

With this type of house it is undoubtedly true that infiltration is markedly less in summer than in winter for the following reasons:

> Wind velocities are lower, especially in sultry weather when the need for dehumidification is greatest.
>
> Outdoor-indoor temperature differentials are much less in summer.
>
> Window sash fits more snugly, and probably the whole wooden structure of the house is tighter in summer.

Hence the customary methods used by heating and ventilating engineers for calculating winter infiltration do not apply in summer.

The "Calorider" and a 250-gallon steel tank to receive spent "Caloride" solution are situated at the foot of the basement stairs shown at *f* and *g*, respectively. The tank is calibrated for volume and hence the amount of "Caloride" liquefied during any selected period can be determined.

The ducts leading from the house space to the "Calorider" are arranged so that the return grilles are in a suitable position to remove "cold floor" in the winter whenever the humidistatic control calls for operation. For this reason the return grilles are located at the foot of the front hall stairs at *a* and at the far end of the living room at *b*. The return ducts are hung on the ceiling of the basement and the direction of air flow is shown by the arrows. The two discharge grilles are under a window seat in the bay window of the dining room at *c* and in the second floor hall at *d*, respectively. The duct to the former is hung from the basement ceiling and the one to the latter passes up through the corner of hall closet 4 at *e*. The spaces served by these four grilles are always open to one another both winter and summer and are called the "base space."

For winter heating the house is equipped with standing radiation using partial vapor system running from about 0.25 pound pressure to about 8 inches mercury vacuum; the boiler is heated by an oil burner. The house is not heated by hot air from the "Calorider" because of the lack of suitable ducts, but sufficient hot water is circulated through its radiator and coils to supply the latent heat of evaporation of the water for humidification and to heat the air after humidification to discharge it at about 75° F. and 50 per cent relative humidity. The air is humidified and washed by contact with water or preferably with calcium chloride solution and make-up water added to maintain its volume constant. In winter the blower on the "Calorider" is operated by a combination of wall humidistat and Windowstat to hold the moisture content of the air at the maximum without permitting objectionable fogging or frosting of the windows. In summer the control is solely by the wall humidistat.

The base space includes second floor halls 9 and 10, first floor halls 3 and 5, living room 1, and dining room 2. The volume of this base space is as follows:

Space 1	2770 cu. ft.
2	1582
3,4	935
5	177
9	1541
10	499
Total	7504 cu. ft.

At various times during summer days the bedrooms are opened to the base space, depending upon the occupancy. If all of the bedrooms are opened simultaneously, the total volume conditioned is 13,688 cubic feet. The total bedroom volume is:

Bedroom 6	1125 cu. ft.
7	1000
8	1768
11	1003
12	1288
Total	6184 cu. ft.

The volumes of the spaces are all net; i. e., the volumes of the partitions and walls themselves are not included. The vestibule, closets, and bathroom volumes are not included. Hence, the maximum volume purposely conditioned at any one time is about 15,000 cubic feet.

Dehumidified air was discharged to the basement space at times to prevent moisture condensation and for drying the laundry on rainy wash days. The volume of the basement is 3800 cubic feet.

The attic is provided with a blower to give nighttime ventilation of the house and is so arranged to cross ventilate the attic in the daytime to carry away the sun load.

Quiet room fans were used on high wall brackets to provide adequate motion to the dehumidified air. If the house had been provided with ducts to each of the rooms for winter heating, these fans would not have been required since the blower normally used with such ducts would have given sufficient air motion.

The normal routine of summer operation of the "Calorider" and the attic blower, described in the preceding paper, was followed.

Definition of Terms

"Calorider conditioned time" in the summer is the total number of hours during which the "Calorider" was under the control of the humidistat; that is, the elapsed hours between the time the humidistat setting was reduced to set the unit in operation, and the time it was increased to prevent operation. The "Calorider conditioned time" does not include the hours of operation of the attic blower during which relief from discomfort was obtained, mostly at night, by bringing into the rooms large volumes of outdoor air. Nor does it include the time when the attic blower was used during the day to ventilate the attic.

"Calorider operating time" in the summer is the actual number of hours that the "Calorider" blower and pump were turning over. This was determined accurately by the cumulative kilowatt hours consumed for any selected period divided by the power used per hour during continuous operation.

"Total conditioned time" is the total number of summer hours during which relief from indoor discomfort was provided by the equipment.

Space is not available here to report the detailed data collected on the test residence over the period of the four summers. Furthermore, the weather varies from year to year, and yearly figures are misleading unless they are carefully evaluated upon the meteorological data. The four years involved include a rather dry summer such as 1936 as well as those that were more humid.

From these results it appears that a "Calorider" capable of treating 750 cubic feet of air per minute in a residence comparable to the structure described and located in an area of similar atmospheric conditions will use, for an average summer, 2000 pounds of "Caloride", 17,000 gallons of city water with a maximum temperature of about 75° F., and 110 kilowatt hours of electrical power.

Careful estimates show that the delivered cost of "Caloride" should not exceed 40 dollars per ton, and under average conditions the total cost of "Calorider" operation for an average summer will be in the neighborhood of 50 dollars. To this should be added the cost of operating an attic blower, which should not exceed 10 dollars for the summer.

Under these conditions the amount of "Caloride" consumed will average about 12 pounds per "Calorider operating hour", which is equivalent to the removal of about 10.2 pounds of water per hour of operation, or a "Calorider operating time" of 167 hours. The "Calorider conditioned time" averages about one and three quarters times its "operating time", or a "Calorider conditioned time" of 290 hours. This does not include the time during which relief from discomfort is produced, especially at night, by the attic blower which about triples the 290 hours of "Calorider conditioned time." The water removed per hour is a measure of occupancy, tightness of house construction, and absolute humidity difference between outdoor and indoor air. The experience obtained with an earlier form had shown that it was unnecessary to take in outdoor air through the "Calorider." This is undoubtedly due to the thorough washing of the air by a viscous solution, accompanied by deodorization and the constant removal of the solution from the unit. The occupancy during the daytime seldom exceeded six persons. The kitchen load was segregated.

For a relatively dry summer such as 1936 the "Caloride" consumption would be reduced to about 1750 pounds and for a more humid summer such as 1937 the amount used would be increased to about 2250 pounds. Cyclic weather forecasting indicates that for the next few summers the higher quantity will be needed.

The above figures are based upon the assumption that the air in the house will be maintained at from 40 to 55 per cent relative humidity by the "Calorider" when the dry-bulb temperature is high concurrently with uncontrolled high humidities. A relative humidity below 35 per cent is not recommended in summer. Frequently in many localities very disagreeable conditions are experienced when the dry-bulb temperatures do not exceed 75° to 77° F. but the atmosphere is nearly saturated with moisture. At these temperatures relative humidities of 60 per cent are acceptable by comparison with unconditioned spaces. This condition is easily produced by direct dehumidification, whereas moisture removal by refrigeration causes dry-bulb temperatures that are too low without reheat.

Commercial Installations

Units using lump "Caloride" have been installed in addition to the test residence for the purpose of obtaining further data. Several of these are described here.

TELEPHONE EXCHANGES. Two installations of "Caloriders" of this same construction have been used in telephone central offices of the manually operated type, one on Long Island and one at a Virginia coast city.

The former contains 47,000 cubic feet of space, divided equally between the operating room and the terminal room on the floor below. In the operating room are situated the switchboards for local and long distance calls, with accessory equipment attended by twenty operators for about 11 hours and by four operators for the rest of the 24-hour day. The terminal room contains the safety relays, thermal protector coils, bell ringing machines, coils, and other accessories attended by an average of three persons throughout the 24 hours. The building is of brick and concrete construction with steel window sash.

The effect of high humidity is reflected in the operation of the equipment. The thermal protector coils in the terminal room are exceedingly fine fuses. When these are in an atmosphere of, say, 65 per cent relative humidity or higher, they will "blow" and thus cut off the service for that particular line. Their normal function is to protect the equipment from power surges, such as lightning strokes. An examination of a blown protector will show whether the cause was lightning or dampness. In years previous to 1935 most of the protector coil troubles were shown to be dampness blows. Other equipment, such as switchboard cables and line and cutoff relays, are also badly affected by high humidity.

In the operators' room humidity adversely affects the switchboard cables, cords, and plugs and results in false busy signals, fading or blurring of speech, buzzing, interrupted service, and connection failures.

Previous attempts to correct humidity conditions were made by turning on the heat in these rooms. In the terminal room this method was partially effective, but in the operators' room it had little effect other than to so lower the efficiency of the girls that service was even worse.

A 500-cubic-foot-per-minute "Calorider" was installed in the spring of 1935 with discharge and return ducts connecting it with the two rooms. The purpose of the installation was primarily for the protection of equipment and secondarily to provide personal comfort. It was found by experience that the relative humidity should be maintained below 60 per cent.

The effect upon equipment is shown by comparing the records for the 1934 summer, during which no dehumidification was provided, and 1935 by the following results: In 1934 there were one hundred and four protector coil troubles, mostly from dampness blows; during 1935 such troubles were reduced to fifteen, of which thirteen were due to line surges and not to dampness. In 1934 line and cutoff relay troubles totaled eight, and in 1935 there were none. In 1934 there were thirty-one cord and plug failures which led to the complete replacement of approximately 200 cords in the operating room as a precautionary measure, whereas in 1935 there were only eleven minor cord troubles and no replacements at all. In 1934 there were two switchboard cable failures in which the trunk crossed with the battery and gave false busy signals for 6 weeks; in 1935 no similar troubles were experienced. During 1936, 1937, and 1938 this operating improvement was consistently maintained.

The consumption of "Caloride" from May 1 to October 1 each year was as follows:

1935	5400 lb.	1937	7500 lb.
1936	3600	1938	4000

Water and power figures were kept for 1935 and indicate that the ratio to "Caloride" consumption was similar to that in the test residence. The maximum water temperature was 72° F.

The chief operator was permitted to open the windows at will whenever the relative humidity was below 55 per cent, with the instruction that when this exceeded 60 per cent they were to be closed. Light and bell signals were provided to announce such conditions. The windows were equipped with fly screens which reduced the free area considerably.

The Virginia telephone exchange installation was made in the summer of 1936. The problem was similar to that of the Long Island exchange in that humidity had been causing failure of apparatus and discomfort of employees. The building is of two-story brick construction with steel window sash; it has a volume of 50,000 cubic feet divided equally between the terminal room and the operating room. Occupancy consists of four men in the terminal and thirty girls in the operating room for 11 hours per day, and an average of six total persons for the remainder of the day.

At the time the installation was ordered, the conditioning load to be carried was unknown, but a 500-cubic-foot-per-minute unit was available and installed for test purposes. Observations during the latter part of the summer showed that the air handled by this unit was insufficient for the purpose. In 1937 a unit with a larger blower delivering 1000 cubic feet per minute was substituted.

In this exchange the unit was operated to prevent voltage leakage—namely, the potential lost by the terminal wires through damp insulation to the grounded frames in the exchange and other places. In this particular exchange good conversation requires that this leakage should not greatly exceed 6 volts. Conversation is progressively poorer up to 14 volts; above this point the leakage causes objectionable transmission. Just prior to the installation of the unit in 1936 the leakage was more than 20 volts. Within 4 hours after the exchange was dehumidified to 50 per cent relative humidity, the leakage was reduced to 12 volts and thereafter reached the selected level of 8 volts; this condition was maintained for the rest of the summer. Beneficial results in other respects were similar to the Long Island exchange.

From August 1 through October 15, 1936, the "Caloride" consumption was 5800 pounds. The maximum water temperature was 84° F.

The radiant heat reflected from the uninsulated flat roof of the operating room made it advisable to provide for dry-bulb reduction for the operators' comfort. Therefore, in 1937 three half-ton room-refrigerating units controlled by their own thermostats were distributed in the operating room.

The 1000-cubic-foot-per-minute "Calorider" in 1937 ran on continuous control by a humidistat set at 50 per cent. The temperature in the operators' room was prevented from exceeding 80–83° F. by the room coolers, as compared to 88° F. for the previous summer. The temperature in the terminal room, not affected by the room coolers, never exceeded 83° F. and the relative humidity was about 45 per cent. Voltage leakage was held to less than 8 volts.

During the one day the "Calorider" was off for a few hours for rearrangements, the room coolers cooled the air passing through them only 6° F. and the room temperature rose to 89° F. The humidity rose to 65 per cent, and some moisture condensation took place on the refrigerator coils. When the "Calorider" was returned to service, the humidity was reduced to 50 per cent within one hour, the room temperature dropped to 83° F., no moisture condensation took place on the cold coils, and the air passing through the coils was reduced 13° F. in temperature. Independent control of both dry-bulb temperature and relative humidity was furnished by this combination of units.

During the 1937 and 1938 humid seasons the amount of "Caloride" consumed averaged 5 tons per year. The greater consumption reflects the more humid atmospheric conditions and longer use in a southern coast town over a northern locality for otherwise similar conditions.

The lack of suitable warehouse and delivery facilities has made the cost of "Caloride" at these points too high to evaluate the true cost of owning and operating further units. It is hoped that this will be rectified in the near future. The advantage of humidity control in telephone exchanges, however, has been demonstrated.

The removal of dust from air is important in telephone exchanges and in other spaces. The impact of air-borne dust upon the viscous liquid films produces remarkably clean air. From this standpoint the process is equivalent to testing methods used for counting dust particles where viscous liquids are employed. Tests run upon ground and bolted silica whose particles rarely exceed 50 microns in diameter have shown 94 per cent removal of the number of particles present in the incoming air. The particles escaping in the discharged air were below 5 microns in diameter, averaging 1 to 2 microns in size. When these escaping particles were collected and returned to the inlet air, to imitate the effect of recirculating the air in a conditioned space, the percentage removal was better than 90 per cent. Dust particles of larger size or shape, such as lint, are more easily and completely removed in one passage. The dust is carried out of the apparatus along with the spent solution.

Several dehumidifying units have been used in nonattended telephone exchanges with similar beneficial results. These exchanges are generally housed in small brick buildings which are inspected once a week. Since many of them do not have running water, the "Caloride" is used in a simple uncooled chamber equipped with a blower. There is no occupancy load, and infiltration is at a minimum. The cost of operation is far below the method previously used—namely, electrical heaters to reduce the relative humidity.

OFFICES. One "Calorider" installation was made in a New York City office in August, 1937, and was operated during the remainder of that summer and during the summer of 1938. The volume of the office is 5000 cubic feet, and a blower was installed to deliver 450 cubic feet per minute. The occupancy was four to five persons during 8 hours per day. The humidity was maintained at 35 to 45 per cent. The total "conditioned time" was 215 hours, and "operating time" was 132 hours for the 33 days during which the unit was run from June 13 to September 1, 1938. The "Caloride" used amounted to 1675 pounds.

MISCELLANEOUS. In order to determine the applicability of dehumidified air for several types of demand, installations of 1000-cubic-feet-per-minute lump "Caloriders" were made for conditioning a beauty parlor, a synthetic resin manufacturing plant, a vacuum mail tube distributing system and a government seed propagation laboratory. In all these cases the "Caloriders", operating continuously under high water removal rates as high as 45 pounds of moisture per hour, were mechanically satisfactory and were replaced in two cases by liquid regenerative units when these were ready for installation. This method of proving the advantages of dried air for various purposes is inexpensive, inasmuch as installation costs are at a minimum and, should the conditions prove satisfactory, regenerative "Caloriders" of larger capacity and lower operating costs can be substituted. If desired, units of the latter type will deliver air at a lower relative humidity—namely, as low as 17 per cent.

The apparatus described in this paper is covered by issued and pending patents in the United States and foreign countries.

Production of "Caloride"

NUMEROUS suggestions have been made for using calcium chloride of various compositions in solid form for drying air and other gases by direct contact. It may be produced as an anhydrous solid or with one, two, four, or six molecules of water of crystallization, generally as a mixture of any two successive hydrates. Anhydrous calcium chloride will absorb more water to complete deliquescence on a weight basis than the hydrates. The monohydrate comes next in the series from this standpoint, but these two forms are costly to prepare and may be dismissed for economic reasons. The same may be said of the solid hydrates containing water greatly in excess of two molecules. Hydrated calcium chloride in flake form will coalesce in storage when its calcium chloride content is appreciably less than about 78 per cent. Common practice, therefore, is to produce flakes approaching all dihydrate, which contains 75 per cent calcium chloride, on a chip machine and then heat them in a rotary kiln through which hot air is passed to increase the calcium chloride content to 78–80 per cent, at which it is a mixture of the mono- and dihydrates containing no tetrahydrate.

Form of Calcium Chloride Desired

Commercial flake calcium chloride is objectionable in air conditioning for various reasons. It contains a considerable proportion of fine particles which, when dumped from a container, are likely to deposit on surfaces outside the air-conditioning unit and liquefy as droplets. The size of voids between original flake particles is too small to permit air flow without excessive pressures, and at such pressures the finest particles are prone to pick up in a dry air stream and be discharged into the air.

A practical method of obtaining large voids in the piled material can be provided by using it in lump form. Broken lump calcium chloride is commonly made by flowing a molten mass containing about 73 to 75 per cent calcium chloride onto a floor; after solidification it is broken up into lump form. This gives a product made up of irregular shapes and sizes, including fine chips and dust. The irregularity of the larger sizes is an objectionable feature; moreover the fine particles must be screened out and the fines reworked before the product is suitable for drying air by direct contact. If the product is to be crushed and screened while cold, these operations must be performed in a dry atmosphere to prevent it from becoming moist. Otherwise the moist lumps will tend to stick together in the shipping containers after surface crystallization takes place. Such a method is unduly cumbersome and expensive. Not only do the lumps so produced vary in size, but the shapes of approximately equivalent size also vary greatly, and many present sharp, jagged points. These points may break off during handling of the shipping containers to produce chips and fines which are objectionable for air-conditioning purposes. If shipped in waterproof bags, the bags may be punctured by the sharp protuberances.

Various methods of forming calcium chloride lumps of varying degrees of hydration have been tried. Lumps which are nonporous, of uniform size, shape, density, and crystalline structure, and which contain about 72 per cent calcium chloride may be satisfactorily and economically manufactured, and are suitable and highly efficient for use in apparatus described in the two previous papers (*1*, *3*).

When molten calcium chloride of this strength is poured into individual molds of the desired size and shape, it is difficult to fill each mold and yet leave no excess that has to be recovered and reworked. Difficulty is also encountered in removing the lumps from the molds and in keeping the walls of the molds free of adhering calcium chloride which interferes with subsequent molding. The lumps cast in this way often contain shrinkage cavities; and whether made in individual molds or cast in slabs which are later crushed to form lumps, the crystalline structure, composition, and density may vary considerably. These variations may occur not only within a lump but also when one lump is compared with another. Some of the lumps or parts of them may be primarily dihydrate and others primarily tetrahydrate, owing to separation during quiescent crystallization; for that reason they exhibit varying rates of liquefaction upon exposure to the flow of moist air. It is important to provide lumps for this purpose which liquefy mainly at the surface and as uniformly as possible; it is also essential that each lump shall liquefy in the same manner.

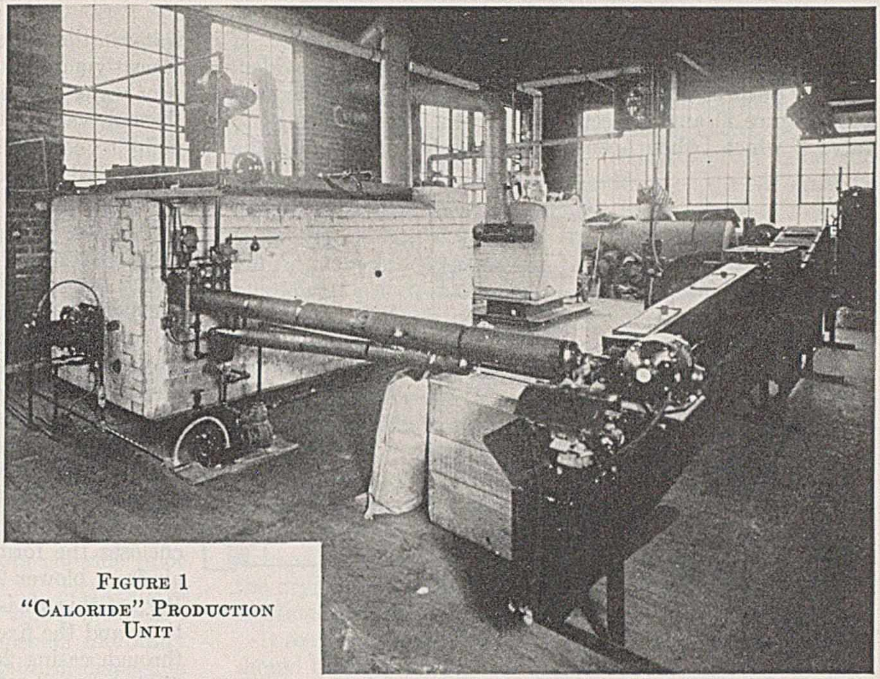


FIGURE 1
"CALORIDE" PRODUCTION UNIT

Attempts have been made to produce uniformly sized and shaped lumps of calcium chloride of uniform composition by granulating and compressing flake calcium chloride in tableting machines. Such lumps contain fine internal passages which communicate with their external surfaces, and they tend to soften and deform under a heavy moisture-absorption load when the weight of the overburden lumps bears upon them. This may be partly overcome by compressing the granules at an elevated temperature at which they are more or less plastic, but equipment limitations introduce difficulties.

Apparatus for Producing Uniform Lumps

A method and apparatus have been devised to produce nonporous lumps of uniform composition and uniform size which are inherently strong enough to stand rough handling without producing an objectionable amount of fine particles. The apparatus is inexpensive to install and provides a continuous process of low operating cost. Practically no fine material is formed as a by-product which would otherwise require reworking.

Figure 1 shows an installation, and Figure 2 is a diagram of the layout of an apparatus. Figure 3 is a longitudinal section of the agitated crystallizing tube with accessories, and Figure 4 a section of the forming and cooling belts.

Tank 1 (Figure 2) may be used as an evaporator to boil off water from more dilute solutions or merely as a reservoir for maintaining the charge of approximately 72 per cent calcium chloride in a boiling condition. The material supplied to the tank may be received at full strength from other evaporative equipment or it may be solution recovered from nonregenerative "Caloriders" as described in previous papers.

Tank 1 may for convenience be heated by an oil burner as shown in Figure 1. The heating is regulated to keep the charge boiling at about 172° C. This is not the true boiling point since solutions of this strength tend to superheat. If the temperature exceeds this point, fresh solution is added. For this purpose a thermostatic bulb is immersed in the tank at 2 (Figure 2) and is electrically or otherwise connected to valve 3 which, when opened, feeds fresh solution into the tank. The solution may be preheated in coil 4 which may be placed in the stack surrounded by flue gases. The steam is led off through vent 5. Instead of supplying solution to the tank, solid calcium chloride may be substituted with the occasional addition of water.

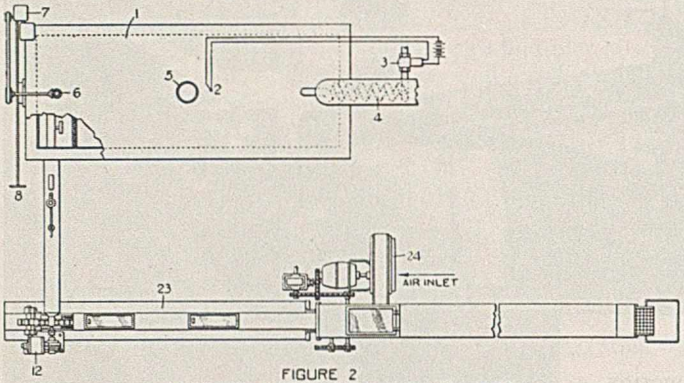


FIGURE 2
LAYOUT OF APPARATUS FOR PRODUCING "CALORIDE"

A small immersed pump is located in the tank at the bottom of shaft 6 and driven at an adjustable speed by variable-speed drive 7. The rate of pumping can be regulated by the operator by means of a conveniently placed handwheel, 8, to suit the rate at which the material is carried away by the continuous forming belt described below.

The pump discharges the molten material through a jacketed crystallizing tube, 9 (Figure 3), which is internally agitated by a rotating and scraping form of agitator, 10. While passing through tube 9, the molten material is cooled quickly to form fine crystals of dihydrate which are thoroughly mixed with still molten mother liquor by the overlapping scrapers, 11; at the same time the scrapers keep the interior surface of tube 9 clear of crystal deposits to facilitate rapid heat transfer. This effect produces a mixture of fine suspended crystals. The agitator is driven by the motor and reducing gear assembly, 12.

The mush or thick slurry is discharged from the tube through opening 13 into the cubicles between the flights of the articulated forming belt, 14, which is enclosed in housing 15. The mushy material so produced is of such consistency that the mass will not flow out through the small openings of the articulated forming belt. The crystals do not settle or segregate during further cooling therein. In this way a fine and uniform crystalline structure is produced and preserved.

During the passage of the material through tube 9, the temperature drop rarely exceeds 12° C. while the latent heat of crystallization of the separating dihydrate is being removed. This latent heat of crystallization can be removed far more rapidly than if the mass were in a quiescent condition, and hence the production capacity of the unit is high. The heat is absorbed by circulating a cooling liquid, preferably water, under 50 pounds gage pressure through jacket 15 surrounding tube 9 by means of pump 16. The heat may be removed from the water by a suitable cooler in pipe line 17.

When the apparatus is shut down, the calcium chloride is ordinarily permitted to solidify in tube 9. Upon restarting, the calcium chloride is softened sufficiently by heating the water in the jacket to permit the agitator to be started. This is neatly accomplished by an electrical immersion heater, 18. Any water that is lost from the circuit may be replenished through valve 19, or water may be admitted slowly at this point to cool the recirculating water. The temperature of the cycled water may be recorded or controlled by thermometers 20 and 21.

Forming belt 14 (Figure 4) runs at a constant speed, and the delivery of the pump in tank 1 is regulated to fill the spaces between the flights. From this standpoint the pump becomes a measuring device since little pressure is required to force the crystallizing mass past the rotating agitator, whose design was selected to impose little or no resistance to flow. Any momentary excess of material delivered to the forming belt is scraped back into the spaces between the flights by a surface scraper at 22 which also smooths off the tops of the individual masses. The open sides of the cubicles between the flights of forming belt 14 are closed by fixed side walls for a short distance from the filling point. Casing 23 encloses the forming belt through which a blast of cooling air from blower 24 (Figure 2) enters through 25 (Figure 4). Part of this air is blown to cool the surfaces of the cast sections and the fixed side walls, and the remainder passes out through casing 26. As the forming belt moves toward the discharge end, the individual masses are sufficiently case-hardened by cooling to retain their shape before they have passed the ends of the fixed side walls. The formed masses in belt 14 finally reach driving sprocket 27, are kicked out of the forming belt by the action ofi ts links, and fall onto a coarse wire mesh belt, 28. This belt moves at a lower speed through casing 26 where the lumps pile up and are further cooled by the blast of air from blower 24. Belt 28 also serves to remove any fine particles, resulting from the breaking off of thin edges from the lumps when they drop from forming belt 14 onto belt 28. A trough is hung under forming belt 14 and wire mesh belt 28 in which the fine particles become cool enough to liquefy by absorption of moisture from the air and the solution is occasionally returned to tank 1. By the time the lumps reach the end of belt 28 they are sufficiently strong to stand dropping into moistureproof containers but are still warm enough not to be deliquesced by the ordinary air used for cooling them.

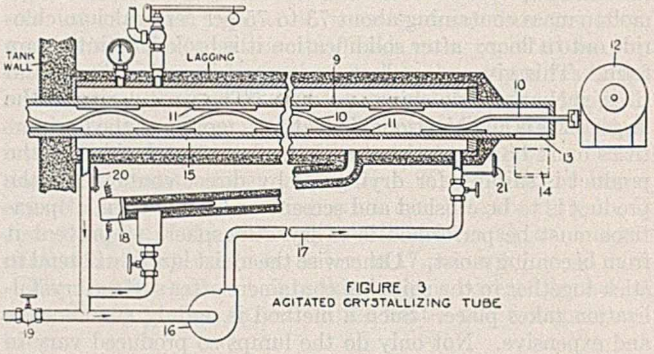


FIGURE 3
AGITATED CRYSTALLIZING TUBE

The lumps as delivered warm from wire mesh belt 28 continue to harden upon further cooling in tight containers, and reach their final strength after 15 to 30 hours, depending upon the bulk of the mass. When finally aged, they exhibit a fine crystalline structure. Cavities in the lumps are rare, and the latter liquefy uniformly at their surfaces when exposed to air flowing at a high velocity. Deliquescence takes place solely at their surfaces (not internally) as a result of the absence of fine channels.

Composition of Lumps

The following table shows the percentage of dihydrate and tetrahydrate corresponding to the percentage of calcium chloride:

% $CaCl_2$	% Dihydrate	% Tetrahydrate	% $CaCl_2$	% Dihydrate	% Tetrahydrate
75	96.6	3.4	71	69.7	30.3
74	89.9	10.1	70	62.8	37.2
73	83.1	16.9	69	56.1	43.9
72	76.3	23.7	68	49.4	50.6

The apparatus as shown in Figures 2, 3, and 4 produces lumps of cubical form, but, by the use of suitably designed forming belts, rods, slabs, and other shapes may be made.

We have found that calcium chloride produced as a by-product in the manufacture of soda ash is suitable for the purpose. However, when air to be conditioned is passed through beds of lumps made from this material and discharged into restricted spaces, a musty or wet plaster odor is noticeable. This has been overcome by the addition of activated carbon since the odor is not inherent in the calcium chloride itself but is due probably to impurities arising from its production. In practice the activated carbon in finely divided form is added to the molten calcium chloride prior to pumping it through crystallizing tube 9. Dry carbon powder will not mix well with the melt, but if it is moistened to form a paste or slurry, it can be dispersed uniformly throughout the mass by agitation. This uniform dispersion is preserved by the method of manufacture, and each finished lump possesses its proportionate amount of carbon. Upon liquefaction during use, the carbon accumulates upon the lump surfaces as a thick sludge and removes odors that would otherwise be discharged into the conditioned air. As further deliquescence takes place, the excess carbon drains from the lump surfaces; since it is easily kept in suspension in the liquid because of the high gravity of the latter, it is still available as a deodorant when the liquid is used for treating air before final contact with lumps.

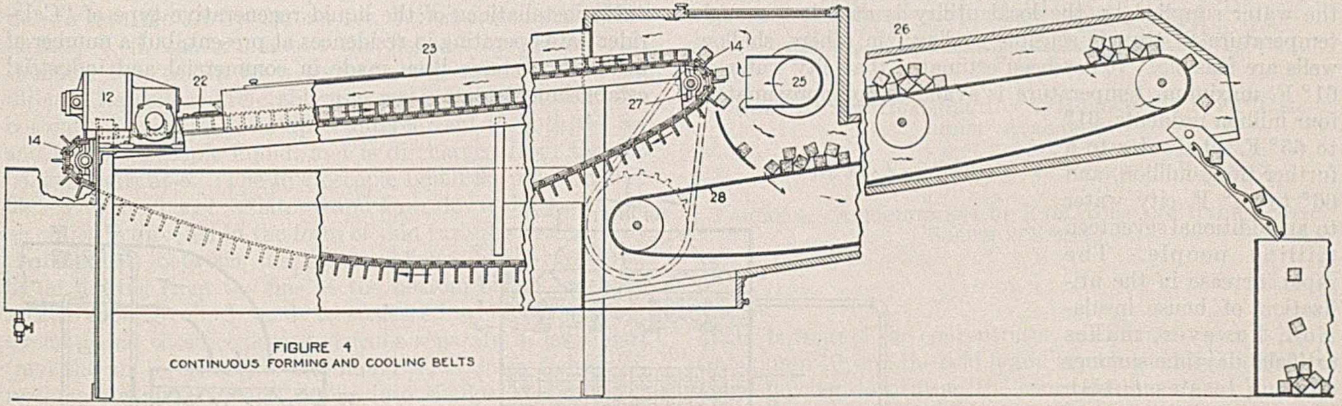


FIGURE 4
CONTINUOUS FORMING AND COOLING BELTS

Lumps used for drying gases or air where odor is not concerned may be produced and used without the addition of carbon. The type of carbon used, however, is cheap and does not increase the cost appreciably.

Uses

Storage rooms, vaults, and boxcars used for holding or shipping materials such as seeds, paper, films, sheet metals, fine metal parts, and other products which are adversely affected by humid air, can be kept sufficiently dry at low cost by the use of lumps of this kind. They may be placed in perforated containers provided with a reservoir to collect the liquefied material. With such an arrangement the moisture diffuses into the voids of the bed of lumps. For this purpose the lumps are far superior in form to flake calcium chloride. They are also free from fine particles that are likely to be deposited upon the materials to be kept dry when a shipping container is dumped into the receptacle used for holding them. Where foods such as table salt, dry cereals, crackers, nuts, milk powder, and the like are concerned, activated carbon should be present in the lumps. When the space is of considerable size and the relative humidity of the air must be held at a constant level throughout the space, it is desirable to provide a fan to circulate the air through a bed of the lumps; for this purpose the fan may be controlled by a humidistat placed in the space. It is preferable to cause the air first to contact the solution produced by liquefaction of the lumps before coming into contact with the lumps themselves. This dilutes the solution for economy and at the same time reduces its crystallizing temperature. When the amount of moisture to be removed hourly is small, it is not necessary to remove heat from the apparatus by outside means. In that event the outlet air is at a somewhat higher temperature than the air of the space. This is not objectionable—for example, in nonattended automatic telephone exchanges. Apparatus of this type has been used to facilitate the drying of freshly laid wall plaster. Marine and tropical locations are noteworthy examples requiring the drying of air.

It seems probable that material in lump form as described should be useful in shelters to protect the civilian population from air raids. The form of apparatus to be used would depend upon the size of the shelter, the expected occupancy, and the length of time calculated for the duration of air raids. The design and proposed treatment of air in such shelters has been discussed recently by Pallot (*4*). From this paper and the accompanying discussion there appears to be no simple standardized solution to this tremendously important problem. Because of necessary limitations, comfort would have to be sacrificed in preference to adequate protection from high explosive or gas bombs.

When dried and cleaned compressed air is required for various purposes, lumps of this type may be placed in a container in the compressed air line. This container may be used as an equalizing tank and should be equipped with a solution drawoff and a suitable eliminator. Because of the open character of a bed of such lumps and their slight resistance to air flow, they may be placed in a container, and air may be drawn through the bed—for example, by the action of a centrifuge used for filtering or separating materials adversely affected by atmospheric moisture. Where storage tanks or bins are used to hold liquids or solids that must be kept dry or free of condensed moisture, the lumps are placed in receptacles attached to the breather openings.

Lumps of hydrated calcium chloride of this type dissolve easily in water since they permit free circulation of liquid as compared to similar material in flake form and are especially suitable for preparing brine solutions. They have been found useful in the thawing of ice in gutters and downspouts of buildings where damage is caused by restricting the runoff of water under certain conditions not infrequently arising in winter.

The process described in this paper is adaptable for the economical production of other crystallizable materials than hydrated calcium chloride when uniformity of shape, composition, and structure of solid forms is desirable.

The product, process, and apparatus are covered by U. S. patents (*2*) and by foreign patents and pending applications.

The Regenerative "Calorider"

THE first two papers of this series (*1*, *3*) dealt with the subject of conditioning air, especially for suburban residences and other relatively small spaces, by means of a "Calorider" of the nonregenerative type using calcium chloride in lump form for dehumidifying air in summer. The same apparatus may be used for heating and humidifying air in winter. Our objective was to devise a cheap and compact unit for this double function where the equipment cost for relief from summer discomfort would not appreciably exceed the cost of indirect warm air equipment for winter heating. The use of an attic blower for nighttime cooling is recommended. The dehumidifying apparatus itself will cause no appreciable dry-bulb reduction of the space in the daytime unless cold water is available. In some localities the water supplied by the local utility is at a low enough temperature to provide sensible cooling; in others, shallow wells are feasible. It has been estimated that city water at 61° F. maximum temperature is available to approximately four million residents, 61° to 65° F. city water to a further three million, and 66° to 72° F. city water to an additional seventeen million people. The rapid increase in the utilization of house insulation, however, makes artificial daytime summer cooling less essential. The simplicity of construction of the nonregenerative unit combined with an attic blower permits a low installed cost and economic operation for small and medium size residential or similar spaces.

For large houses whose owners require day and night wet-bulb reduction and can afford to pay for independent dew-point and dry-bulb temperature control equipment, a lower hourly operating cost can be obtained with a regenerative type of "Calorider." This type employs low-temperature heat, such as low-pressure steam, to maintain the liquid used for absorbing moisture at a suitable concentration. The steam, or even hot water at 180° F., can be supplied by the house heating boiler or by an independent heating means using oil, coal, or gas as the fuel. If dew-point reduction alone is sufficient, the air may be discharged at the proper relative humidity and give a comfort effect comparable to that obtained by the nonregenerative type "Calorider" described previously. If dry-bulb reduction is also required, any suitable cooling means, such as well water or mechanical refrigeration, can be employed. If this is arranged to cool the air after it has been dried, the cooling coils for this purpose do not have to carry the latent heat load. The combined equipment is then controlled by a space humidistat for moisture control and a space thermostat for temperature control, each independent of the other. Another variation, which will generally be found to be more economical, is to use a hygroscopic liquid which will produce superdried air—say with a relative humidity of 15 to 25 per cent at temperatures of, for example, 75° to 85° F.—and then partially rehumidify this air by evaporative cooling to permit the discharge into the space of cooled air at a selected relative humidity. By suitable arrangement of control accessories, both the dry-bulb and dew-point temperatures can be independently regulated. With such a method the sole source of energy, except that for fans and pumps which would generally be motor-driven, is derived direct from fuel.

It should be borne in mind that the average home owner has an aversion to the ownership of complicated machinery that may require attention or repair services. Ultimately the cost of owning and operating units of the regenerative type will undoubtedly be low enough to justify their installation in medium and large size homes, but for most small houses only the lowest first-cost installation will be purchased, such as a nonregenerative "Calorider" combined with an attic blower.

No installations of the liquid regenerative type of "Calorider" are operating in residences at present, but a number of installations have been made in commercial and industrial establishments.

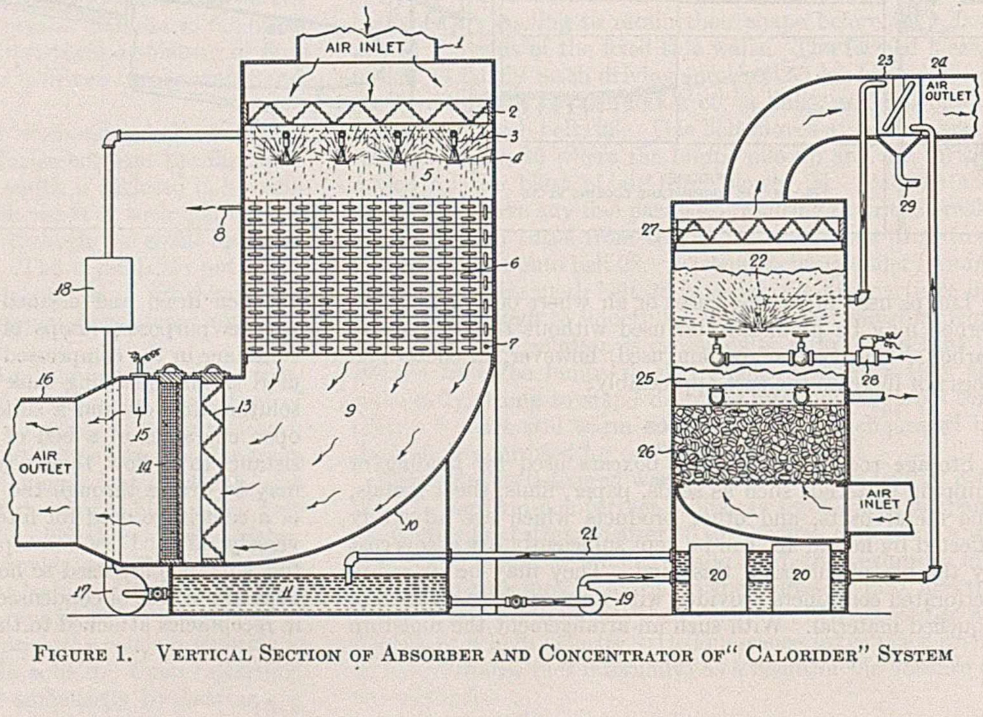


FIGURE 1. VERTICAL SECTION OF ABSORBER AND CONCENTRATOR OF "CALORIDER" SYSTEM

Reference was made in the second paper of this series to the liquid-phase air-drying section of the nonregenerative "Calorider." This constitutes the absorber section of the regenerative units, and the object of this paper is to discuss the novel principles employed in the absorption of moisture and the regeneration of the hygroscopic solution.

Figure 1 is a vertical section of a regenerative unit for drying air. A vertical type concurrent flow absorber is shown on the left and a concentrator on the right for maintaining a suitable strength of the hygroscopic solution. This type of absorber has certain operating advantages and is preferred if the headroom in the space is sufficient to accommodate it.

Figure 2 shows a section of a horizontal absorber for installations lacking sufficient ceiling heights for the vertical type. In this unit the air and solution flow in a horizontal but concurrent direction. Figure 3 is a vertical cross section of Figure 2 taken through the finned-tube radiator. Figure 4 shows another arrangement of radiators and hygroscopic solution sprays in a horizontal type absorber.

Figure 5 is a vertical type "Calorider" absorber, such as is shown in Figure 1, for treating 6000 cubic feet of air per minute (360,000 cubic feet per hour) at low pressure. The absorber is shown at the left. The blower at the right draws the air through the absorber and discharges it to the conditioned space.

Figure 6 shows a "Calorider" solution concentrator in the foreground with its blower, connections, pump, and control panel, and in the background the absorber shown in Figure 5.

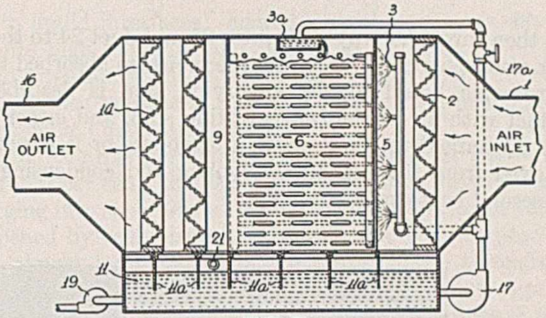


FIG.2.

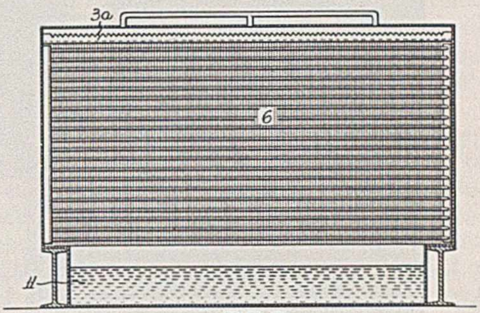


FIG.3.

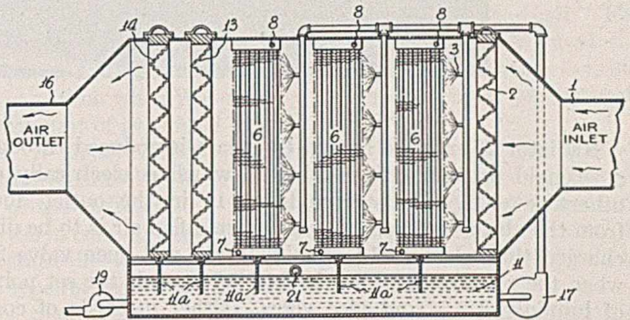


FIG.4.

FIGURE 2. VERTICAL SECTION OF HORIZONTAL TYPE "CALORIDER" ABSORBER

FIGURE 3. VERTICAL CROSS SECTION OF FIGURE 2

FIGURE 4. ARRANGEMENT OF RADIATORS AND HYGROSCOPIC SOLUTION SPRAYS

Cyclic Principles of the System

AIR-DRYING AND SOLUTION RECONCENTRATION STEPS. In the arrangement shown in Figure 1 the air entering the absorber at 1 may all be drawn from the outdoor atmosphere or from the conditioned space or from both sources. It first passes through a back-drift spray eliminator, 2, into contact with the suspension of droplets of the hygroscopic liquid thrown into the air by the nozzles, 3, and the impingement targets, 4, in space 5 above the finned-tube radiator, 6. Radiator 6 is cooled by a coolant, such as water, passing through its coils. Preferably the water enters at 7 at the bottom set of coils, flows up countercurrent to both the air and the hygroscopic liquid, and is discharged from the top bank of coils at 8. The hygroscopic liquid is spread in thin films over the fins of radiator 6 and flows down along with the air which is directed in the form of thin turbulent streams by the channels between the radiator fins. The hygroscopic liquid flowing from the fins at the bottom of the extended surface cooling coil, 6, tends to coalesce into relatively large streams, and these coalesced streams separate in large part from the air in space 9. The liquid flows down the air directionating plate 10 and drains into shallow reservoir 11. Any droplets of liquid still suspended in the air stream are separated by spray eliminators 13 and 14, and the cleaned air passes in contact with humidistat 15 on its way to air outlet 16.

The solution in reservoir 11 is discharged by pump 17 through strainer 18, if it is desired to remove suspended dirt, to spray nozzles 3. A second pump, 19, draws solution from reservoir 11 and discharges it to the concentrator. In practice a single pump is ordinarily used with the discharge split to proportion the amount of liquid pumped to the absorber and the concentrator. For ordinary purposes about one sixth as much solution is pumped to the concentrator as is recirculated to the absorber, and both circuits flow continuously as long as the system is in operation. Various forms of heat exchangers have been used, but in this example an extended surface heat exchanger, 20, is immersed in a sump at the bottom of the concentrator. This receives cold liquid from pump 19, and the cold liquid is preheated by the warmer liquid flowing down from the concentrating step. The prewarmed liquid then flows either direct to spray nozzles 22 or through a second heat exchanger, 23, in duct 24. The preheated liquid is sprayed over and flows down through the extended surface radiator, 25, where it is heated and partially concentrated, and then continues down through packed section 26 in which it is cooled by further evaporation, and thence into the sump for further cooling by heat exchanger 20. From the sump the concentrated liquid, at a temperature closely approaching that of the liquid discharged by pump 19, returns to reservoir 11 of the absorber. There it enriches the hygroscopic solution which, in turn, is pumped to sprays 3.

The concentrator preferably has its own blower, which draws air either from outdoors or from the conditioned space, and discharges it up through the packed section, 26, and the heating radiator, 25, countercurrent to the descending liquid and then through spray eliminator 27 and duct 24 to the outdoor atmosphere. In this way the moisture absorbed by the hygroscopic liquid in the air-drying step is desorbed by contact with air in the concentrating step, and either all of it is discharged to the outdoor atmosphere or it is partially removed from the hot air by cooling and condensing it in the second heat exchanger, 23.

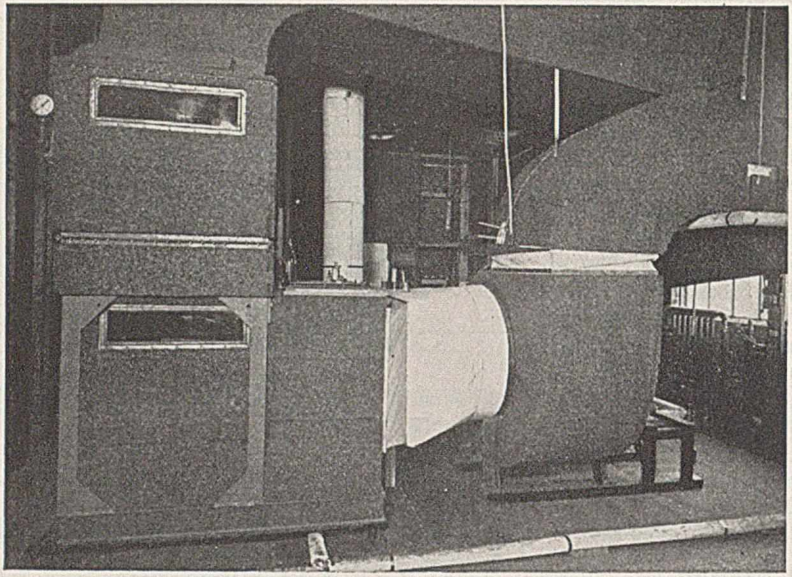


Figure 5. "Calorider" Absorber for Treating 6000 Cubic Feet of Air per Minute

Radiator 25 may be heated by steam introduced through a solenoid or modulating valve 28 which is electrically or otherwise energized by humidistat 15 in the outlet duct from the absorber unit. When dehumidified air is to be discharged through duct 16, humidistat 15 will open valve 28 when the relative humidity in duct 16 exceeds the set point of humidistat 15, and vice versa. Other methods of controlling the concentration of the solution have been proposed, such as means affected by its specific gravity, but for the cycle shown humidistatic control is preferred.

Basic Principles of Each Step. The absorbers shown in Figures 2 and 4 are set up in a horizontal position. The parts are numbered the same as in Figure 1.

Figure 3 shows finned-tube radiator 6 of Figure 2 with vertical fins and horizontal cooling tubes. Despite this fin arrangement, the high velocity of the air causes the hygroscopic liquid to flow concurrently with the air. It is desirable to assure that the fin surfaces are wetted in all parts of the radiator. Where the gravity of the solution is high and the length of the radiator is great, in the direction of air flow a weir, 3*a*, may be used to spread some of the liquid over the top of the radiator fins. Such an arrangement will prevent any lack of a suitable supply of liquid of proper concentration at the top left-hand corner of radiator 6 (Figure 2). In place of weirs, sprays may be used if proper care is taken to baffle the space between the roof of the casing and the top of the radiator to prevent air from by-passing the latter and thereby escape treatment. Baffles 11*a* are provided to stop short-circuiting of the air past the bottoms of the radiator or the eliminators above the liquid in reservoir 11. Valve 17*a* may be used to supply the correct flow of solution to the weir.

Figure 4 also shows an absorber through which the air passes in a horizontal direction and by its velocity carries the liquid along its path of flow. The radiator is divided into three sections with sprays preceding each section. The cooling tubes are vertical and the fins horizontal. By shortening the radiators and positioning the fins horizontally, ample wetting of all fin surfaces is obtained and preserved by means of sprays 3.

In this example (Figure 4), baffles 11*a* below the radiator sections may be repositioned and extended to the bottom of the reservoir to form separate compartments, and the solutions used in each radiator section and its associated compartment may be kept separate and recirculated by independent pumps to the corresponding radiator section and to a separate concentrator. In this way solutions of progressively increasing strengths or of varying compositions may be used in successive sections. Suitable entrainment eliminators should be used preceding each set of spray nozzles under this modification. Successively colder zones may be produced by flowing the coolant through the series of radiators from left to right, or independent coolants may be used in the separate radiator sections.

Absorber Principles

The absorber may be designed to treat a fixed rate of air flow and deliver it at a fixed but adjustable relative humidity. The temperature of the discharge air may or may not vary, depending upon whether the inlet temperature of the coolant is fixed or is variable, and hence the total heat content of the discharge air may be constant or variable. The total heat content of the inlet air may also be relatively constant or continually fluctuating, depending upon its source, but generally it is far more variable than that of the outlet air. If the inlet air is obtained largely from the conditioned space, it is more likely to be constant than if taken from outdoors, but there are exceptions. The heat load to be carried by the absorber is the difference in total heat content of the inlet air and the outlet air, since it is understood that the total heat content removed is the sum of the latent heat of condensation of the absorbed water and the sensible heat removed from the air. It is clear that the heat load may vary from hour to hour and even during much shorter time intervals. The absorber is normally designed to handle the maximum heat load but it is also highly desirable that it be able to compensate automatically for any fluctuations as quickly as possible and perform with high efficiency under any reasonable conditions. The type of absorber described here approximates this ideal requirement closely.

The description of its operation will have to be limited to a fixed set of conditions. Let us assume that only outdoor air is drawn into the absorber. The outdoor air is taken at standard maximum design conditions of 95° F. dry bulb, 78° wet bulb, and 72° dew point. The total heat content is 41.3 B. t. u. per pound, of which 18.5 B. t. u. represents the latent heat and 22.8 B. t. u. the sensible heat above 0° F. The temperature of the coolant is assumed to be constant at 70° F. We will also assume that the temperature of the discharge air is fixed at 75° F. and its relative humidity 40 per cent. The total heat content of the discharge air is 26.3 B. t. u. per pound, made up of 8.3 B. t. u. of latent heat and 18.0 B. t. u. of sensible heat. The total heat load to be carried by the absorber is therefore 15.0 B. t. u. per pound of inlet air. We will also assume that the volume of inlet air is 6000 cubic feet per minute or 440 pounds of air which requires the removal of 6600 B. t. u. per minute or 396,000 B. t. u. per hour. Of this total amount, 70 per cent is latent heat and 30 per cent is sensible heat. The heat balances will be discussed later but this suffices to show that a large amount of heat must be removed. Space limitations in buildings require that this be done in a compact unit with a minimum impedance to air flow.

After entering the absorber casing (Figure 1), the air first comes into contact with the solution in finely divided form either as suspended droplets caused by the sprays alone, as shown, or combined with suitable tower packing in space 5. The solution at the sprays is cold; it is at the same temperature as the solution in reservoir 11 which, with good heat transfer provisions in 20, is substantially the same as the coldest solution in the unit—namely, that draining from the bottom of extended surface radiator 6. While passing through space 5 the air is cooled, moisture is absorbed by the solution, latent heat is converted to sensible heat, and the solution temperature is increased because it is not in contact with cooling surfaces. The intimate mixture of the solution and the air passes on into contact with the closely spaced fins and coils of radiator 6. The preliminary contact in space 5 and the resulting rise in solution temperature causes the water discharged at 8 to leave at a higher temperature than would otherwise be the case. This results in an appreciable saving in water or, if a cooling tower is employed, permits the use of a smaller size.

As the thin streams of high-velocity air flow down in contact with the liquid films, further moisture is absorbed and more sensible heat is generated within the films, but this is removed at the moment and place of formation. The concurrent streams of the reacting fluids flow countercurrent to the cooling water so that when the air and liquid separate from each other they are at the lowest temperature reached in the system and are in substantial moisture and temperature equilibrium with each other.

The retention time of the liquid in the radiator is low because the rapidly moving air forces the liquid along; since it is not possible to flood the channels, the velocity may be high which enhances the rate of heat transfer to the cooling coils. By providing a suitable ratio of coil surface to fin surface and proper velocity for the coolant, the over-all heat transfer rate may be very high.

Since the sensible heat formed is practically instantaneously removed by the coolant, the amount of hygroscopic liquid which must be pumped through the apparatus is only a small fraction of that required were the heat to be carried away to a separate cooling zone by the liquid itself. In fact, only sufficient hygroscopic liquid need be circulated through the radiator to prevent undue dilution by the absorbed water.

The very large area of fins which can be accommodated in a small volume of radiator exposes correspondingly extensive gas to liquid interfaces; combined with cooling *in situ*, this permits high moisture and heat transfer rates. The small liquid retention of the device makes sensitive control possible and likewise permits a reduced investment when high-cost hygroscopic liquids are used.

When the relative humidity of the outlet air shows a rise above 40 per cent, this is an indication that the solution discharging into space 9 has become too dilute. Steam valve 28 is opened by humidistat 15 and partially concentrated solution almost immediately begins to discharge through pipe 21 into reservoir 11, and the small amount of solution present there starts to become enriched. The quick response to this demand upon the concentrator depends upon its retention of circulating solution but this is of small volume. This concentrating effect is reflected quickly in the strength of solution to sprays 3 and also in the solution in final contact with the air in space 9. Hence under low total heat load conditions there is very little lag or overrun.

Under high heat load conditions, such as the example given above, the concentrator continues to enrich the solution to the sprays (especially if a modulating valve is used at 28) until it discharges into space 9 at a suitable strength to reduce the relative humidity of the outlet air to the set point of humidistat 15. It should be borne in mind that concurrent flow of air and solution permits as high a concentration of solution discharged into space 5 as is necessary to establish equilibrium conditions at the downstream face of the radiator. When the moisture content of the inlet air is high, the concentration of the solution in space 5 is also high. This causes the greatest temperature rise of the solution at this point, and hence the cooling water exit temperature is raised at a time when it is called upon to carry away an increased amount of generated heat.

If highly variant, the heat load on the absorber may require control of the rate of flow of cooling water to the coils of the radiator, but this is merely a question of calculating the maximum required and equipping the unit with a thermostatically controlled valve, preferably of the modulating type for regulating the flow at reduced loads.

Should the inlet air vary rapidly in moisture content, this method permits a sensitive selective control of the outlet air quality and the conservation of cooling water.

The solutions generally used may be defined as viscous liquids, and since the films on the radiator fins pass into space 9, they coalesce into streams and separate easily from the air stream. Any small portion entrained in the air as fine droplets is easily separated from it by suitable eliminators. When chloride salts are used to form the hygroscopic solution, the perfection of spray elimination can be tested by the use of silver chromate paper in the discharge duct after the blower. This test is extremely sensitive to very slight traces of chlorides. It is stated to be capable of showing even the small salt content of the atmosphere in coastal regions.

One unexpected advantage of concurrent flow of air and solution in the absorber resides in the observation that with viscous solutions there is a markedly lessened tendency to form foam than when countercurrent flow is used.

Concentrator Principles

The concentrator has been particularly designed as a cooperative companion to the absorber, but its characteristic features may make it useful for other purposes as an independent unit. It may be much smaller than the absorber, and the air volume passed through may be one seventh that treated in the absorber because the temperature spread between the solution in the concentrator and the heating fluid is far greater than the temperature difference between the absorber solution and the coolant.

We have designed the concentrator to remove water from the solution into an air stream because this permits the use of low-temperature heat which is generally cheaper or more readily available than high-temperature heat. Where salts are used to form the hygroscopic solution, they are nonvolatile, and it is necessary only to ensure against entrainment losses. Low-temperature concentration of such salt solutions minimizes corrosion.

It is advantageous to return the concentrated solution to the absorber circuit at a temperature not greatly in excess of the solution therein; otherwise the heat load on its coolant is increased. The temperature reduction of the heated solution is obtained in two steps. First, the hot solution draining down from heating radiator 25 is evaporatively cooled by contact with a countercurrent of upward-flowing air in packed section 26, and the solution partially cooled there is further cooled by heat transfer in heat exchanger 20. In this way the solution returning through pipe 21 should not exceed the temperature of the solution in space 9 by more than a few degrees. Despite the small volume of solution in reservoir 11, this is not heated to any marked extent, but even if it should be, the treated air in space 9 is prevented by plate 10 from contacting with and being rehumidified by the solution in the reservoir. If the solution discharged at sprays 3 should be warm for the same reason, the desired equilibrium of the treated air and solution as they separate from each other in space 9 is not disturbed. Such a result should not be permitted to take place, but if it should, the only penalty is that more heat release is required in the absorber. With countercurrent flow of air and solution, however, a warming of the solution at the sprays—namely, where the air and solution would separate in space 5—would upset the absorber design conditions.

The cooling of the solution by evaporation in packed section 26 of the concentrator depends upon the dew-point temperature of the entering air. It is also promoted by air of lower temperature but to a lesser extent. Under almost all conditions, outdoor air is suitable for this purpose, but a greater cooling effect can be obtained by taking air from the conditioned space. Such spaces require ventilation; and where outdoor air is dried and discharged into the space by the absorber, the amount required for ventilation is generally large compared to that needed to operate the concentrator. The use of such air in this concentrator permits operating economies.

When steam valve 28 is opened or closed, the blower attached to the concentrator air inlet may likewise be started and stopped. Ordinarily, however, this blower is permitted to operate continuously; for if it does, the concentration of the solution continues after valve 28 is shut off due to the residual heat left in radiator 25 and other structural parts. Evaporative cooling of the returning solution in packed section 26 likewise continues. It is preferable for pump 19 to continue the recirculation of the solution through the concentrator, for with salt solutions this prevents the formation of deposits upon the radiator surfaces.

In the general description it was stated that the solution from heat exchanger 20 may be discharged direct to sprays 22; but if the cost of heat or other considerations justify the investment, a second heat exchanger, 23, of the finned-tube type may be inserted in the hot moisture-laden air passing out through duct 24. By this means, both sensible heat and latent heat may be regained and the condensed water withdrawn through 29. This distilled water may be used for a variety of purposes.

The discharge of hot air containing large amounts of moisture through duct 24 to the outdoors may, under certain circumstances as to location and atmospheric conditions, cause a local disadvantage or a nuisance. In such cases the use of heat exchanger 23 may be justified, and the cooled air of reduced moisture content may be discharged direct to the outdoors. Instances are sometimes met where it is difficult to install a duct connecting the concentrator to the outdoor atmosphere. In such cases the air leaving outlet 24 may be passed through a cooling coil to condense out further moisture and the air may be recirculated to the concentrator air inlet.

Low-pressure steam may be used in the concentrator. Often in factories, exhaust steam is available at low cost and this is suitable for the purpose. Since heat is the principal source of energy required for the system, the operating cost may frequently be very low. The system may be arranged to absorb 1 pound of water with a steam use as low as 1.3 pounds. For comfort conditioning where large amounts of fresh air would be desirable—for example, where the occupancy is high—the operating cost is sufficiently low so that a major portion of the air to be treated may be drawn from outdoors rather than recirculated from the space. However, even the part of the air that is recirculated is thoroughly scrubbed by a viscous dehydrating solution which has been cycled through the hot concentrator in contact with air. This undoubtedly produces a marked pasteurizing effect, except perhaps upon some spore-bearing organisms.

Control of the Space

The foregoing description of the operation of the absorber and concentrator assumes that the relative humidity of the discharge air at a temperature dependent upon the available coolant is of primary concern. It will be shown later that this relative humidity generally remains fixed, regardless of the discharge temperature, when the composition and concentration of the solution is selected and maintained. At lower temperatures the absolute humidity will be less, and vice versa. When air is to be used as a process material, its quality may be specified either as to its absolute humidity or its relative humidity. Its absolute humidity may be controlled by fixing both the relative humidity and temperature of the outlet air. Where relative humidity alone is concerned, the control may be solely by a humidistat in the discharge duct from the absorber. Even for certain air-conditioning purposes this type of control is adequate—for example, where a large part or all of the air is taken from outdoors and discharged into the space to provide much ventilation. Under other circumstances the space itself should be under humidistatic control. This is necessary when a large part of the air is taken back from a space in which moisture is generated or enters through infiltration from outside. In that event the space itself may be considered for all practical purposes as a part of the duct system, and humidistat 15 may be placed in it. Humidistat 15 in the dehumidified air of the space then controls the amount of heat introduced into the concentrator. The latter then supplies solution to the absorber at such a strength that the air around the humidistat is reduced to the selected relative humidity. Under certain circumstances two humidistats may be used, one in the space and one in duct 16. The latter then overrides the former as a safety device to prevent the solution from becoming too concentrated as it returns from the concentrator.

If dry-bulb reduction of the space cannot be attained by the available coolant supplied to the absorber, independent means such as refrigeration can be used to cool the space. This may be accomplished by cooling the air in the main discharge duct or by separate air-cooling units in the space. Then the moisture content of the air can be controlled humidistatically and independently of thermostatic control of the space temperature. Where it is expensive to lead ducts through an existing building or where zone control is required, there may be several suitably placed absorbers supplied by solution from a single concentrator. Other variations in application are feasible, such as producing superdried air and adiabatically vaporizing water into it to obtain dry-bulb reduction of the space. This double function can be controlled by a space thermostat acting upon the evaporative water supply and a space humidistat acting upon the concentrator. As the space temperature starts to rise, the evaporative water inlet is opened by the thermostat which, unrestrained, would cause a rise in the relative humidity of the space. The humidistat, sensing this rise, however, causes the concentrator to produce a more concentrated solution. The air leaving the absorber is then dried sufficiently to evaporate enough water for cooling the space without increasing its relative humidity. When the prescribed dry-bulb and wet-bulb conditions are satisfied, the process maintains them until a change in the load calls for a reversal of the steps.

The discussion so far has been concerned with the removal of moisture from air, with or without sensible cooling. In winter, humidification is often a necessity or desirable. Some applications require a high humidity at all times. This has often been supplied in the past by live steam jets. Other processes prefer a more or less constant humidity, but its level may be relatively unimportant. For example, in color printing the relative humidity may be high or low but should remain constant. In the past this condition has been set up by humidifying the working space in winter to approach that of the humid season. Condensation on external walls in winter causes structural damage, and secondarily, the drying of the ink itself is retarded. It is therefore desirable to operate at a relative humidity that will obviate these troubles. A good compromise seems to be about 50 per cent relative humidity if adequate provision is made against structural damage. In that event the humidifying system installed may be supplemented by an air-drying unit, and the humidistatic controls may be set to operate each apparatus in turn. The absorber may be inserted in the duct system ahead of the present steam jets and the air drawn through it continuously, or the ducts may be separate circuits. If a very narrow range of control is required or if for any reason the use of live steam is objectionable, this can be done more satisfactorily by the hygroscopic solution itself. This is provided for very simply by using the concentrator as a heater to supply heated solution to the absorber to humidify the air, during which cycle air is not blown through the concentrator and coolant is not passed through the radiator coils in the absorber. The air passing through the absorber becomes heated and moistened, and water is added to the reservoir by a float valve to hold the volume of solution constant. When the humidity of the space is raised to the desired point, a humidistat shuts off the concentrator steam valve. If the humidity in the space should later rise above a fixed point for any reason, the humidistat starts the concentrator air blower, opens the steam valve, and permits the coolant to flow through the absorber radiator coils. It is assumed that air is passing through the absorber at all times to the conditioned space. By a proper design of the space humidistat, the points at which humidification stops and dehumidification begins, and vice versa, can be separated to any desired extent. In Figure 6 a control board is shown in the background which operates the system to give year-round control of humidity by utilizing these principles. Because of the small volumes of liquids and the relatively small size of the apparatus, the method is sufficiently sensitive to respond to minor changes in conditions.

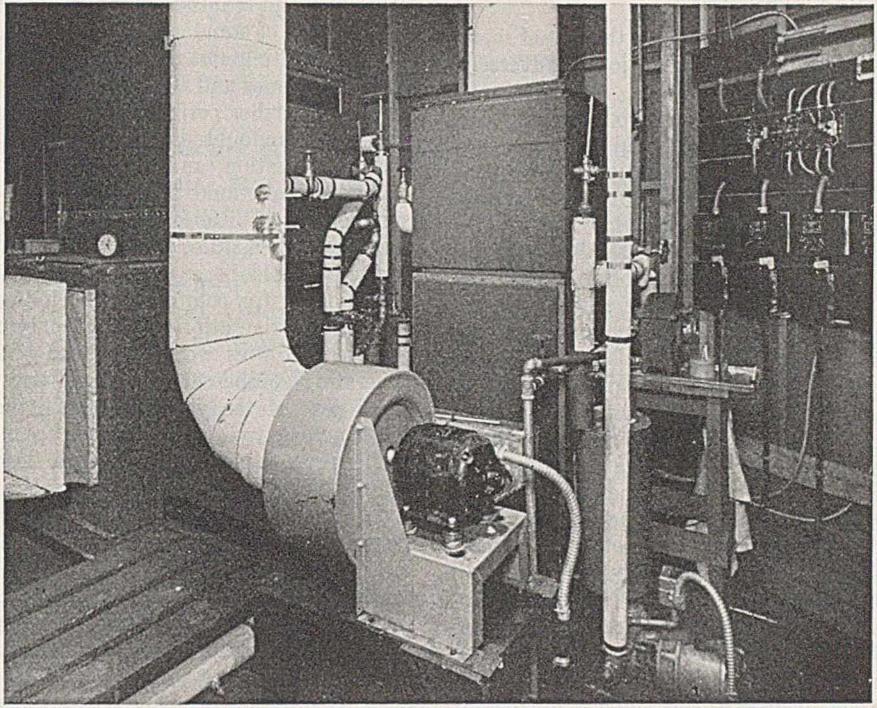


FIGURE 6. "CALORIDER" CONCENTRATOR IN THE FOREGROUND AND ABSORBER IN THE BACKGROUND

Fields of Application

The maintenance of a selected relative humidity of the air as it leaves contact with the liquid in the absorber under dynamic conditions closely approximates the theoretical value under static conditions. When the air is being dehumidified, the relative humidity is slightly greater than theoretical, and vice versa. The following figures are examples of minimum relative humidities of air discharged from this type of equipment when operating at approximately atmospheric pressure:

Solution	Relative Humidity of Discharge Air
1. $CaCl_2$	40
2. $CaCl_2$-$CaBr_2$[a]	25
3. $ZnCl_2$	15

[a] Ratio $CaCl_2:CaBr_2$ = 1:5.3 parts by weight.

Higher relative humidities merely require the use of more dilute solutions. Gases other than air that do not adversely affect the solutions can be treated.

Where lower relative humidities are required, the absorber can be operated at reduced temperatures and the gas or air reheated after dehydration, or the dehydration can be performed at higher pressures, followed by reduction to lower pressures. In general, however, where very low absolute or relative humidities are necessary, the use of solid adsorbents such as silica gel and activated alumina are often preferable.

In the majority of industries, solutions of suitable vapor pressures can be selected to dry air at atmospheric pressures, deliver it to the working space, and create satisfactory manufacturing conditions. Some of the products or processes which require the regulation of the moisture content of the factory air are listed; the desired relative humidity range for them is from 20 to 50 per cent, with temperatures varying from 70° to 85° F. or somewhat more in most of the following examples: baking powder, chewing gum, confectionery, cork molding, cosmetics, drugs, electrical products, explosives, film drying, macaroni, macaroons, malt starch, matches, paper storage and processing, photographic plates, rubber dipping, storage of sheet metals, sugar, tobacco, and cigars.

Testing laboratories require special conditions within and outside of these ranges. Dried air may be required for special purposes, such as in egg drying, leather shoe drying, and pneumatic tube mail and parcel conveyors. Dried air as a process material would be advantageous, for example, for linoleum manufacture, linseed oil processing, and blast furnace operations. The drying of compressed air used, for example, in mining operations for the generation of power in expansion engines below ground is promising.

To this list should be added the drying of natural gas, a large part of which is already being treated with triethylene glycol as the hygroscopic liquid, and of coal gas. Coal gas drying is not yet practiced in this country but is being carried out in practically all English undertakings.

Many of the products listed above are made in factories already equipped with electrical refrigeration for condensing moisture out of the air and then reheating the dried air when necessary. In some industries this method has made little headway because of the prohibitive equipment cost or uneconomical operating charges.

It is believed that the cost of electrical refrigeration equipment will be difficult to reduce to any marked extent even with mass production, whereas direct dehumidification of air, either by solid adsorbents or by hygroscopic solutions, is a newcomer and reduced equipment costs are more likely when some degree of standardization is attained.

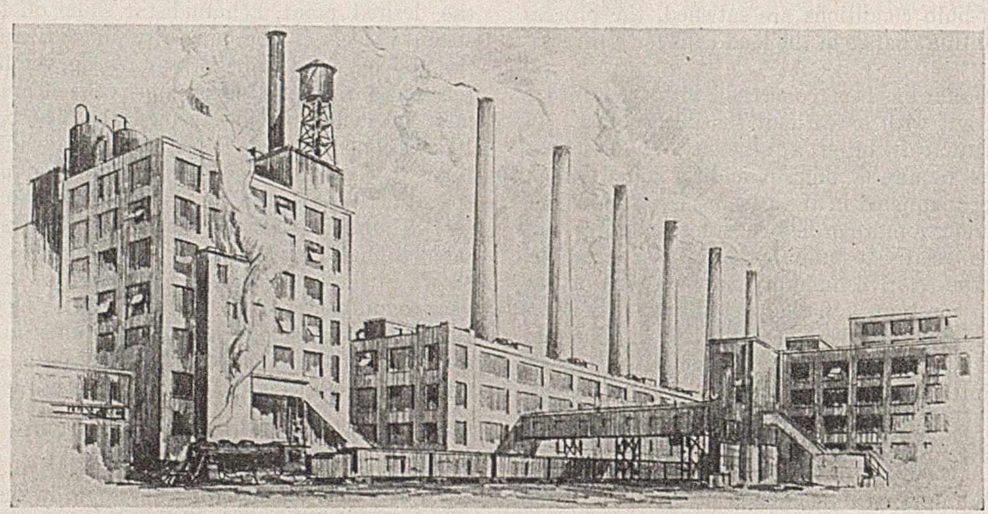
The operating cost must be viewed from two angles—that of the consumer and of the public utility supplying electrical energy. Further perfection in electrical refrigeration equipment will undoubtedly be made toward somewhat lower energy utilization, and power rates will continue to be reduced if year-round load factors are not disturbed. The summer air-conditioning demand for power, however, comes at a time when other uses are generally at the year's peak. If there should be any widespread adoption of summer air conditioning for comfort or for industrial purposes, and if electrical refrigeration were the only method available, the electrical utilities would be faced with a demand for new generating equipment whose sole use would be largely in a small part of the year. Such a situation would probably force increased year-round power rates to all consumers.

The reverse picture is true if a large part of the air-conditioning load can be taken up by the direct use of heat derived from coal, oil, or gas where increased summer use would be welcome to the fuel suppliers. In many instances a lower operating cost is possible by direct dehumidification; the market is thereby broadened and the number of installations increased. Each installation will require power, and the most convenient form is electrical energy. By this means the electric utilities will share in the development without being unduly burdened. There should be no antagonism between the two methods but mutual assistance. Such is the promise of direct dehumidification.

The process and apparatus described in this paper are covered by United States and foreign patents and applications.

Literature Cited

(1) Downs, C. R., Ind. Eng. Chem., 31, 134 (1939).
(2) Downs, C. R., U. S. Patents, 2,027,093 (1936); 2,154,671–2, and 2,154,708 (1939).
(3) Downs, C. R., and Spiselman, J. W., Ind. Eng. Chem., 31, 681 (1939).
(4) Pallot, *J. Inst. Heating Ventilating Engrs.*, 6, No. 65, 230 (1938).



Gutta-Percha and Balata in Submarine Cable Insulation

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Data are given on the dielectric resistance, electrification, dielectric constant, and loss factor of several groups of natural compositions of the gutta-percha class. Curves connecting the variation of some of these properties with time and temperature, and the effect of additions of one component to another, are included. It is demonstrated that the electrical characteristics of a mixture are not connected with the figures pertaining to the components by a known mathematical relation. The aging properties and methods by which accurate data may be obtained are stated. The general results are discussed in connection with submarine cable requirements, and a plea is made for the alteration of cable specifications in the light of the data available. A basis for such a specification is included.

SUPPLIES of gutta-percha and balata are received from their production centers in different grades and forms. In the main, however, they may be divided into the following groups; by far the largest use to which these materials have been put is in the insulation of submarine cables:

A. Plantation gutta-percha (leaf gutta-percha), obtained from leaves and leaf prunings by mechanical extraction. Malay, Java, and Sumatra are the chief sources, and Palaquium and its hybrids are the trees planted.

B. Tapped gutta-percha, from Federated Malay States Forestry Reserve. Trees are largely *Palaquium oblongifolium.*

C. Jungle gutta-percha, obtained by scraping the gum from the bark after felling the trees. The best grades are obtained from the Malayan trees of the genuine type *Palaquium oblongifolium.* Various other trees and hybrids are employed, and other grades of fair quality are obtained from North Borneo and Sumatra.

D. Sheet balata, obtained by evaporation of the latex in thin layers. Mostly from British and Dutch Guianas from the species *Mimusops globosa.*

E. Block balata, obtained by boiling latex until coagulation occurs and compressing the hot plastic mass into block form. Smoke from wood fires is also introduced as an aid to coagulation. The main sources are the forests of the Amazon districts, Venezuela, Brazil, and Panama.

The first two groups contain products which may be relied upon to yield consistently high qualities; but the others are of jungle origin and collected by native labor, and are very variable in nature. The characteristics of the material are therefore also given in groups in accordance with the above scheme.

Cleaning and Drying

As received, most grades, especially the jungle varieties, require cleaning by a simple process of washing in water. The operation is carried out either in a Universal washer or in a fluted-roll masticator immersed in water. In either case the hot plastic material is masticated for a prolonged period in a constantly changing supply of hot water at the desired temperature until all particles of bark, leaf fiber, sand, etc., are removed. The washing time may vary from 1 to 5 hours according to the variety of the material being cleaned. When washing is completed, the material is strained under hydraulic pressure through a fine metallic gauze to remove any pieces of foreign matter not removed during washing. The material is finally dried by mastication in a jacketed mixer fitted with a vacuum hood. The final moisture content is important and should not generally be reduced below 1 per cent.

Electrical Characteristics

The material may be pressed into disk form under heat, and its electrical characteristics are measured between two plates to form a condenser. Alternatively, the material may be extruded, while hot and plastic, around a copper conductor to form a circular core.

The first method has been employed to a large extent, but there are several objections to its use, particularly when machinery and experience are available to enable the second method to be performed. The results quoted in this paper, therefore, have all been determined from specimens of core.

Among the objections to the disk method, there is the serious risk that in molding the disk, the temperature will exceed 100° C. (212° F.) to obtain a smooth surface. This temperature will cause expansion of moisture and the production of a porous disk. Alternatively, moisture will be lost and the material will suffer accordingly. It is well known that gutta-percha and similar mixtures must be conditioned so that a small amount of moisture is retained in the material; otherwise the aging will suffer. There is also a difficulty in carrying out extended aging tests by the disk method under water or salt solutions, since the sample must be removed and the surface dried before being tested. For these reasons the second method is preferred, especially as the sample is then in a condition almost identical with that of its normal use in submarine cable.

The dimensions of the conductor are obtained by gaging and are checked by an electrical resistance measurement at a known temperature. The outside diameter of the core is obtained by gaging, and the figure is checked by subtracting the conductor weight from the total weight.

If the method is doubted in any way, a simple check may be obtained by determining the dielectric constant upon a disk made from the fully dried material and obtaining the apparent dimensions of the core by obvious calculations. This method is applicable only when the moisture is of the order of 1 per cent. In that case the dielectric constant of the dried specimen will differ from that of the wet by a small and negligible amount.

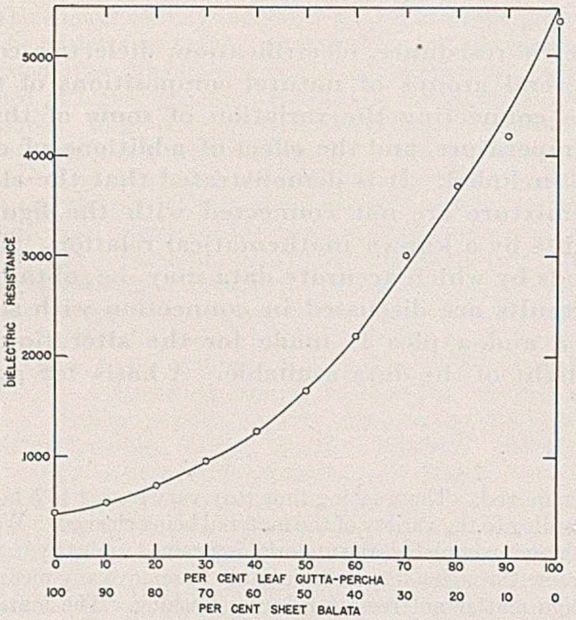

FIGURE 1. DIELECTRIC RESISTANCE *vs.* COMPOSITION FOR MIXTURE OF SHEET BALATA AND LEAF GUTTA-PERCHA MIXTURE AT 75° F.

It would not be desirable in a paper of this nature to discuss at length the merits and disadvantages of the various methods employed in determining the electrical characteristics. Briefly, however, the apparatus may be divided into two classes—direct-current instruments and alternating-current apparatus. The d. c. resistance is measured upon a sensitive galvanometer by direct deflection methods. As is common with most solid dielectrics, there is considerable absorption current during the first few minutes after application of the testing voltage (usually not less than 500 volts), and it is customary in the case of cables insulated with gutta-percha to measure the d. c. resistance after 1-minute absorption or electrification. To obtain a measurement of the absorption, the d. c. resistance is again determined after 2-minute application of the voltage; one hundred times the difference between the two readings, divided by the first, is recorded as the percentage electrification. The d. c. capacity is measured on a galvanometer by ballistic methods.

Alternating current characteristics given here were measured either upon a screened Schering bridge with a Wagner earthing device, or upon a parallel resistance bridge of a modified Wien type. As a standard for comparison purposes, a testing frequency of 2000 cycles per second was adopted throughout this paper, unless otherwise stated. In stating the dielectric loss factor, the ratio G/C is quoted since this is generally employed by submarine cable engineers instead of the power factor. The two constants are connected by the formulas:

$$G/C = 2\pi f(PF) \tag{1}$$

$$PF = \cos\theta \tag{2}$$

where G = apparent conductance of cable, micromhos
C = capacity of cable, microfarads
PF = power factor
f = frequency, cycles/second
θ = phase angle, degrees

Equation 1 is applicable only to small values of PF.

Since gutta-percha and balata are mainly used for submarine cable insulation, the cores to be tested are immersed in water during the test. As will be seen later, the dielectric resistance varies with time from the date the core was made. It is therefore necessary to standardize the time elapsed from the date of manufacture to the time of test; since most specifications call for this period to be 14 days, that time has largely been adopted in this paper.

Aging Properties

In view of the long life expected of submarine cables insulated with gutta-percha, it is necessary for test purposes to adopt some means of forecasting the aging properties of the material. As in the case of vulcanized rubber, it may be demonstrated that the aging of gutta-percha is brought about largely by oxidation. Unfortunately the well-known accelerated tests adopted for rubber are not applicable to gutta-percha and balata, on account of the low temperature (about 50° C.) at which these materials commence to soften. The following test methods were therefore devised by which accelerated aging data may be obtained. No comparison with service results can as yet be made, since it is practically impossible to obtain consistent aging results under service conditions. Comparison with specimens kept in tanks is progressing, however; although far from complete, results appear to indicate that, employed in conjunction with a knowledge of the composition under test, the results of artificial aging may generally be relied upon to give a moderately accurate forecast of the behavior in service. It may at least be claimed that a specimen possessing good accelerated aging properties will behave well in service, and vice versa. Little is as yet known of the type of deterioration which takes place, but it is hoped at an early date to be able to throw more light on this problem.

Dry Heat Test

The specimen is usually a piece of core about 6 inches long, but if not available, a sample with dimensions approximately $^1/_4 \times {}^1/_4 \times 6$ inches will suffice. It is suspended in a dark chamber maintained electrically at a constant temperature of 45° C. (113° F.). The specimen is examined periodically by a hand method consisting of bending the specimen double and making careful observation as to surface cracks. If this test is carried to completion, the specimen will eventually crack through.

It is appreciated that this method of examination is somewhat arbitrary, but if the form and method of making the specimen are consistent and the examination is carried out in a regular manner, the results are sufficiently accurate for routine testing purposes and may be repeated with only a small percentage of error. For more accurate work a series of specimens may be molded for tensile strength determinations and the deterioration measured after the specimens have been submitted to the testing conditions for a standard period of time. The figures in Table I under the heading "Heat Test" were carried to completion by hand examination.

Ultraviolet Tests

A thin specimen 0.006 inch thick is placed on the base of a Hanovia quartz mercury vapor lamp, at a distance of approximately 8 inches from the source of light. The specimen is periodically examined by hand methods until it is easily broken when bent sharply. More accurate results may be obtained by judging the condition of the sample before and after the standard period of time from a determination of its solubility in hot acetone. In this paper the figures were obtained by hand methods, and the tests carried out to completion.

The method is not very reliable when a sample in one group is compared with that from another, since the different resins are affected differently by the actinic rays. In view of the varying emission of ultraviolet light from a quartz lamp, it is advisable to compare all results with a known arbitrary standard and to calculate results to a common standard. In view of the difficulties experienced in standardizing this test, it is subject to serious criticism, but it has its value in that comparative results may be obtained in a few hours only, whereas other tests require days and often months.

Hydrogen Peroxide Tests

Since some specimens are unduly and severely affected by dry heat or ultraviolet light in relation to their life in service, this test has been devised so that data may be obtained in the absence of atmospheric oxygen. A sample 0.006 inch thick is immersed in a 20-volume solution of hydrogen peroxide maintained at 45° C. The sample is removed periodically and examined by hand, as in the ultraviolet light test, and continued until brittleness has been reached. The results are of particular value when fairly rapid data are desired upon samples abnormally sensitive to ultraviolet light. They are, however, liable to yield misleading information when carried out upon samples containing antioxidant. Care must be taken to maintain the requisite strength of hydrogen peroxide.

Experimental Results

Under favorable circumstances measurements on the same sample may be repeated to within 1 or 2 per cent. Yet owing to the varied nature of some of the types of materials and to the lack of supervision during their collection from the jungle, there are occasions when abnormal results are obtained. In these cases it is presumed that the specimen has been contaminated in some way or adulterated with other gums, and those figures which experience shows to be unreasonable and misleading have been rejected.

Because of the wide variation in values from sample to sample, the usual method of showing average figures with their variations has not been used. Instead, ranges have been given and it may be assumed that the distribution of values within these ranges is approximately uniform and not in accordance with the usual curve which has a heavy peak at or near the average value.

Table I represents the abstracted data upon hundreds of samples of each variety, but where the data is limited and the figures variable, the information has not been included. The resin contents are given in Table II.

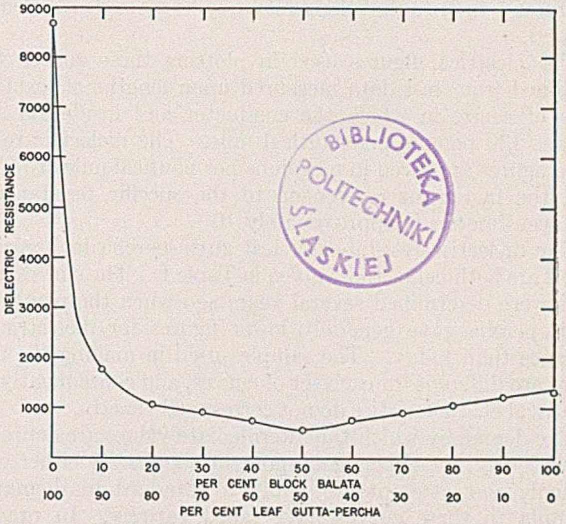

Figure 2. Dielectric Resistance *vs.* Composition for Mixture of Leaf Gutta-Percha and Block Balata at 75° F.

Obviously it is inadmissible to quote cable specifications in detail, but it may be stated that normal cable specifications call for a dielectric resistance of 500 to 2000 megohms per nautical mile, corresponding approximately to a specific resistance of approximately 5 to 20 ohm-cm. × 10^{14}. Furthermore, electrification limits are specified to be between 3 and 8 per cent (more recently the upper limit has been increased to 15 per cent). These figures in no way represent working requirements but are based on what has been obtained in the past.

Table I. Abstracted Data from Tests on Many Samples

		Electrical Characteristics					Aging Properties		
		D. c. at 75° F., 14 days after mft.			A. c. at 35° F., 14 days after mft. at 2000 cycles/sec.				
Group	Name	Resistivity *Ohm-cm.* × 10^{14}	Dielectric constant	Electrification %	Dielectric constant	*G/C*	Heat test *Days*	Ultraviolet *Hours*	Hydrogen peroxide *Hours*
A	Leaf gutta-percha	100–500	3.0	20–50	2.9	40–70	Above 150	40–75	Above 200
B	Tapped gutta-percha	50–200	2.9–3.0	5–25	2.9	50–90	Above 150	40–75	Above 180
C	Jungle:								
	Pahang	2–300	2.9–3.5	1–30	Similar to d. c. values	50–100	Above 150	...	.....
	Bulongan red	70–200	Above 3.2	5–15		High	70–200	...	.....
	Bandger red	Above 100	Above 3.3	5–15		High	....	...	.....
	Mixed varieties	Variable, usually high	Above 3.3	Usually high		350	....	...	.....
D	Sheet balata:								
	British Guiana R. D.	6–25	3.0–3.2	10–20	3.0–3.2	150–250	30–50	15–25	90–100
	Dutch Guiana B. C. S.	3–20	3.0–3.1	8–15	3.0–3.2	100–250	20–50	12–25	70–100
	Unknown origin C. L.	15–80	3.1–3.3	15–20	3.0–3.3	250–350	50–100	20–40	120–200
E	Block balata:								
	Venezuela	4–15	3.0–3.5	12–20	3.0–3.4	120–350	10–30	10–20	100–150
	Brazil	2–6	3.0–3.2	8–18	3.1–3.2	80–200	20–40	15–25	100–150
	Panama	4–12	3.2–3.4	12–20	3.1–3.3	About 150	10–40	10–25	80–150
	Aniba	15–300	3.0–3.5	4–10	3.0–3.5	250–400	Over 90	25–50	150–250
F	Paragutta (*2*)	300–1000	2.6	35–50	2.6–2.7	9–15	20–30	20	Up to 100
	K-gutta (*1*)	500–1500	2.5–2.6	30–60	2.55–2.65	4–10	Above 150	30	Above 250

Table I seems to show that it is impossible to obtain such figures from the components available; in fact the specification, though intended to ensure a good quality mixture, often precludes the use of any but the smallest proportion of the best materials. Fortunately for the cable manufacturer, mixtures of equal proportions of two materials from different groups do not produce electrical characteristics which are the arithmetic means of those of the two components. Frequently the mixture possesses a lower dielectric resistance than either of the materials from which it is being made, and a selection of composition-resistance curves are included (Figures 1 to 3) so that this effect may be more clearly demonstrated.

The electrical figures used in plotting these curves were obtained from test data measured upon lengths of insulated core of a size in which the conductor and insulation each weighs 130 pounds per nautical mile. The dielectric resistance figures are given in megohms per nautical mile at 75° F., and the factor for conversion to the specific resistance in ohm-centimeters is approximately 10^{12}.

The dielectric resistance of leaf gutta-percha in Figures 1 and 2 are both below those given in Table I. The curves however were determined several years ago when the plantation gutta-percha gave generally lower figures for dielectric resistance than today. The samples used in making the mixtures are different for each set of curves, and consequently the electrical characteristics do not correspond exactly.

The degree by which the intermediate values are depressed is obviously not dependent upon the figures for either component, and attempts to apply a standard mathematical formula to these curves have failed entirely. In practice nothing more than approximations to the true results can be forecast; therefore, to obtain the exact figures for a mixture, samples must be made and the characteristics determined. Obviously, as experience is gained, the data will be capable of prediction to fairly close values. But when it is realized that the normal commercial mixture is made of perhaps twenty components and rarely less than ten, the difficulties will be fully appreciated.

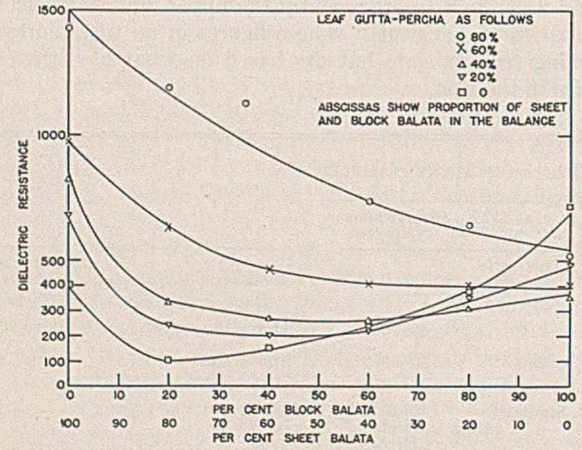

Figure 3. Dielectric Resistance *vs.* Composition for Mixture of Leaf Gutta-Percha, Sheet Balata, and Block Balata at 75° F.

The above points have been stressed somewhat unduly in a desire to show what is perhaps not generally appreciated—namely, the futility of adhering to old cable specifications which are out of date and which are undoubtedly tending to prevent the use of the best materials.

The cable specifications referred to were written around early supplies which were manufactured largely from group *C* and, in the main, from the best items in the group. It would be comparatively easy to formulate a mixture from these components, were they available, which possess the desired characteristics.

In view of the lack of supplies, present-day mixtures must be made from other groups classified in Table I. If the matter ended with meeting specified electrical values, it would also be comparatively simple to provide the components of the mixture from groups *D* and *E*. Aniba, group *E*, which possesses a low electrification percentage, cannot be relied upon, however, to produce a stable product when used in major proportions, and it will be observed that the aging characteristics of groups *D* and *E* are notably poor. Finally it must be remembered that the manufacturer is expected to supply a cable which will function satisfactorily for many years.

Table II. Resin Contents of Cleaned Materials

Type of Material	Resin Content, %
Balata, sheet	45–50
Balata, block	50–55
Leaf gutta-percha	8–12
Tapped gutta-percha (Federated Malay States)	8–14
Jungle gutta-percha (commercial mixture)	35–45

This aim can be achieved by the use of the best materials available from the aging point of view which also possess the best fundamental electrical characteristics. There are two important operational characteristics of a submarine cable upon which the cable speed largely depends and which depend, in turn, upon the fundamental characteristics of the insulating material. These are low capacity and low *G/C* factor; the latter becomes important only at considerable speeds of operation. The dielectric resistance is of little importance provided it is not unduly low. Table I shows that the materials possessing the best aging properties are those with the best fundamental electrical characteristics from the operational point of view, and it seems most unreasonable, therefore, to apply a specification which precludes the use of at least substantial proportions of such components.

Table I clearly demonstrates that the first and second groups possess the lowest dielectric constants and the best aging characteristics. In addition, these products are cultivated under European supervision. The supplies of tapped gutta-percha are limited and somewhat expensive, but the supply of plantation gutta-percha is determined largely by the volume of the demand, and the quality is consistently good.

The use of these materials alone is not necessarily to be recommended, since both are rather harder than normal mixtures. If, however, a specification were drawn up based upon cable requirements and good aging qualities, but not containing clauses limiting the unimportant electrical characteristics, then the hardness of items *A* and *B* could be tempered by a proportion of items *D* and *E*, selected to produce the optimum mechanical and electrical characteristics compatible with good aging values.

Suggested Form of Specifications

Obviously specifications for a new and high-speed telegraphic or telephone cable will be based upon the special conditions of that particular cable. The material used for insulating the center wire will probably be a special one such as those discussed under "Dielectrics for Telephone Cable."

For repair lengths, or short cables, however, such expensive dielectrics are not warranted, and in these cases a specification could be advantageously based upon the following principles:

1. The dielectric shall, except as stated under clause 2, consist entirely of a mixture of gums normally classified as gutta-percha, which shall include balata in its various forms.
2. Small additions of carefully selected waxes, deproteinized rubber, and antioxidants may be added if desirable, but in no case shall such additions exceed 5 per cent.
3. The moisture content shall be such as to be as nearly as possible the optimum for the mixture—namely, that at equilibrium in a 3.5 per cent salt solution. It shall not be less than 0.5 per cent.
4. The dielectric constant of the material, as calculated from the capacity of the core in water at 75° F., 14 days after manufacture and from its dimensions, shall not exceed 3.25.
5. The resistivity of the material as calculated from the dimensions and dielectric resistance of the core determined with a voltage of 500, 14 days after manufacture and after immersion in water at 75° F. for not less than 24 hours, shall be not less than 4 ohm-cm. $\times 10^{14}$.
6. The electrification of the cable shall be smooth and free from abnormalities, and shall be consistent with a faultless insulation.
7. The water absorption of the material determined in a 3.5 per cent salt solution by an approved method shall be not more than 2 per cent after allowing for the initial moisture content of the material.
8. The aging properties as demonstrated by artificial tests with an approved method shall be such as will ensure a faultless insulation with satisfactory aging properties.
9. The examination of a section of the core shall show clearly three separate layers of material and no cleavage which would indicate nonhomogeneous coverings.

Dielectrics for Telephone Cable

Until comparatively recent times it has been assumed that balata insulation is more efficient than gutta-percha at voice frequencies. Unfortunately, however, the test data upon which this assumption was based were determined at 75° F. The sea-bottom temperatures are usually considerably below this figure and approach 34° F. Figure 4, connecting temperature and *G/C* factor, will demonstrate the rapid increase of the latter as the former is reduced. Equivalent curves are included for other compositions; at reduced temperatures balata insulation does not show up favorably.

The rapid rise in *G/C* factor for balata when the temperature is reduced as compared with that of the plantation gutta-percha insulation is connected with the high resin content of the former compared with that of the latter. When the resin is removed, the substances all possess similar a. c. characteristics—namely, a *G/C* factor of approximately 20 at 2000 cycles per second and 34° F., and a dielectric constant of approximately 2.6. The resin contents of the materials are given in Table II. The removal of the resins causes a much more serious loss in the case of balata than in that of gutta-percha.

If, therefore, it is desirable to obtain the optimum electrical characteristics, the resins must be entirely removed from any one or a mixture of the materials, thus employing what is substantially the pure hydrocarbon. In some cases the extraneous matter is difficult to remove by normal washing methods; the hydrocarbon should then be dissolved and filtered. In all cases the latter treatment provides materials with electrical characteristics which are definitely superior to those of material produced normally.

The hydrocarbon alone is rather expensive and difficult to extrude satisfactorily on account of its toughness, and a softening material cheaper than the hydrocarbon was sought. Experiments of different workers resulted in the production of Paragutta (*2*) which consists of 50 per cent balata hydrocarbon, 40 per cent deproteinized rubber, and 10 per cent hydrocarbon wax; and K-gutta (*1*), consisting of 70 per cent hydrocarbon and 30 per cent refined petroleum jelly.

These two substances may be regarded as the best available commercially for insulating long-distance submarine telephone cables. Each possesses a dielectric constant of about 2.6 and a *G/C* factor of about 12. In practice it is found that the hydrocarbon from leaf gutta-percha is more plastic when hot than that from balata at the same temperature, and since leaf gutta-percha also yields a cheaper hydrocarbon, its use is strongly advocated.

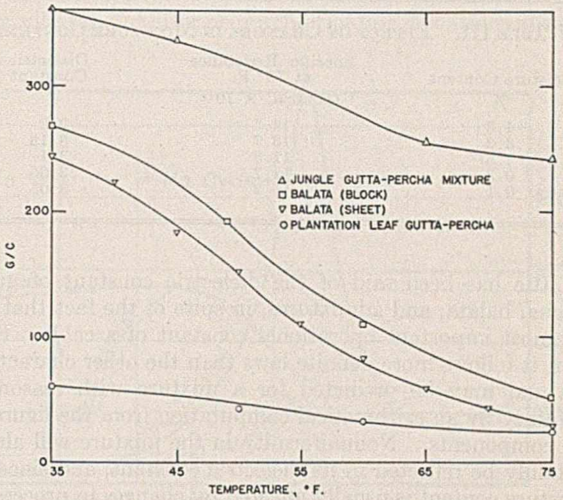

FIGURE 4. COMPARATIVE CHANGES OF *G/C* FACTOR WITH TEMPERATURE FOR DIFFERENT COMPOSITIONS AT 2000 CYCLES PER SECOND

The ideal for either K-gutta or Paragutta would appear to be a mixture of the two hydrocarbons, that from balata to provide toughness, and that from gutta-percha to increase thermoplasticity.

Additional Electrical Data

Mention must be made of other electrical values looked upon as important in the testing of cables insulated with gutta-percha. One of the most important depends upon the fact, already mentioned, that the dielectric resistance will normally show a steady rise in value with time, dating from the time when the mixture was processed. This improvement continues for a considerable period, often amounting to years, before a steady state is reached. A study of a large number of data indicates that it is difficult to compute any definite figure for this characteristic to any one or more types, but the data available are no doubt vitiated by conditions outside normal control. The figures measured are seriously affected by several conditions which are normally uncontrolled, such as purity of water in which the cable is immersed, the minute proportions of affecting substances present in the tar employed in the sheathing operations, and slight variations of temperature not recorded.

It is unfortunate that the data available to an investigator upon this subject are confined to those obtained upon the finished cable instead of upon the core, since such results will be seriously affected by the above-mentioned causes. Isolated cases exist in which data are available upon cores which have been stored in water for prolonged periods and regularly tested. However, when such a subject is being investigated, it is most unwise to depend upon the results of tests taken on one or two cores only. On account of the varying nature of the raw materials, only the average results of a large number of determinations should be used in fixing the normal characteristics of a mixture.

The improvement, then, should not be regarded as a necessary criterion of quality, although it is clear that a steady drop in insulation is most undesirable. Experiments and experience have demonstrated that in certain cases an initial drop in dielectric resistance may be observed; then, provided the core is otherwise satisfactory, the improvement will eventually set in, although possibly at a reduced rate. Additional factors affecting improvement are moisture content of the dielectric and concentration of dissolved salts in the water.

Table III. Effect of Changes in Moisture Content

Moisture Content %	Specific Resistance at 75° F. *Ohm-cm.* × 10^{14}	Dielectric Constant
4.3	13.5	3.2
3.3	13.7	3.18
1.5	11.3	3.1
0.3	11.7	3.05
0.1	14.2	3.05

Little has been said of the dielectric constant of gutta-percha, balata, and admixtures, in spite of the fact that it is the most important operational constant of a cable. However, it follows more definite laws than the other characteristics and may be predicted for a mixture with reasonable certainty by an arithmetical computation from the figures of the components. Nonuniformity in the mixture will almost certainly be reflected in its dielectric constant, and since the moisture content is usually affected by changes in processing, the high dielectric constant of the water will cause changes in the capacity of the finished material.

It might be expected that the dielectric resistance would be more susceptible than the dielectric constant to changes in moisture content; although this is found to be the case, the variations in the former are very irregular, whereas those of the latter are consistent with theory. Table III gives the results obtained in a series of experiments on a mixture of normal proportions in which, as far as possible, the only variable was the moisture content.

Conclusions

The satisfactory insulation of a submarine cable core is fundamentally complicated by the considerable variation in the characteristics of the different types of raw materials. Furthermore, the characteristics of a mixture of components do not bear any known mathematical relation to those of the components. Finally, the considerable variations experienced in sample to sample of the same type of raw material, by reason of their jungle origin, causes still further complication.

In these circumstances, it is to be deplored that cable specifications are drawn up in such a way as to cause still further difficulties to a manufacturer endeavoring to supply the best cables commercially possible.

It is to be hoped, therefore, that this paper will throw some light upon what is generally considered an obscure subject and at the same time cause serious thought by those responsible for drawing up cable specifications.

Acknowledgment

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Literature Cited

(1) Dean, J. N., *India Rubber J.*, 82, 853–6 (1931).
(2) Kemp, A. R., *J. Franklin Inst.*, 211, 37–57 (1931).

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Removal of Ammonia in Water Treatment

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MANY microscopic organisms live and grow in water distribution systems. These organisms are troublesome; they often cause odors and unsightly conditions in the water, although they are nonpathogenic as far as we know. For the latter reason they have not been subjected to much study by medical bacteriologists. Usually they cannot be grown under artificial conditions and therefore are not attractive material for the general microbiologist. However, increased demands for a more perfect water in any public supply requires that these organisms be eliminated as far as possible from the distribution system.

At present, we have little systematic knowledge of these organisms. Most of them are a true and higher form of bacteria (iron and sulfur bacteria), but protozoa and higher organisms, especially nematodes, are also very common. In general three ways are available to eliminate these organisms: avoidance of contamination, disinfection, and elimination of food supply (starvation).

Elimination of Organisms

Avoidance of contamination requires that the organisms be kept out by the filter. The efficiency of the filter in this respect is rather low. Even if most bacteria, spores, and cysts are kept back in the filter and are to a great extent removed from it in backwashing, a few may pass through. It is also known that nematodes can slowly wiggle through the sand and carry some organisms along. Furthermore, other sources of contamination are possible, such as backsiphoning through plumbing fixtures, and eddy currents at leaks and through fire hydrant drains.

Disinfection is produced mainly through chlorination, but all organisms found seem to be very resistant to chlorine; at least they are not affected by a chlorine dosage up to 0.5 p. p. m., to which the water in the distribution system is ordinarily limited because of tastes. Another way of practical disinfection for chlorine-resistant organisms is in the use of the lime softening process. The meager observations made so far seem to show that chlorine-resistant bacteria can resist a low pH but not the high pH produced by the lime treatment. Water softening combined with chlorination gives, therefore, a wide range of active disinfection.

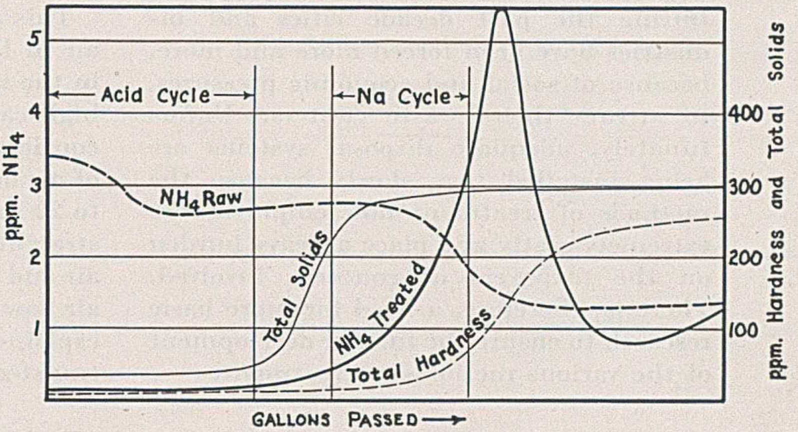
Other means for the limitation of these growths are much needed. It is conceivable that cutting off the food supply will cause their elimination by starvation. All living organisms must have available some food supply which furnishes material for bodily growth and which is also capable of yielding energy through chemical reactions.

Iron organisms gain at least part of the energy needed from the oxidation of ferrous to ferric iron. Similarly, sulfur bacteria use the oxidation of sulfur to sulfate ions or of hydrogen sulfide to water and elementary sulfur. However, in some cases it is found that these organisms or similar ones persist even in the absence of sulfur and with very complete removal of the iron. In such cases attention may be called to the possibility that the organisms may gain energy from ammonia which is present in many well waters. The energy available from the oxidation of ammonia depends on the product formed, as shown by the equations:

$$NH_4^+ + 2O_2 = 2H^+ + NO_3^- + H_2O - 81{,}230 \text{ cal.}$$

$$NH_4^+ + {}^3/_2O_2 = 2H^+ + NO_2^- + H_2O - 63{,}230 \text{ cal.}$$

$$NH_4^+ + {}^3/_4O_2 = H^+ + {}^1/_2N_2 + {}^3/_2H_2O - 86{,}670 \text{ cal.}$$



REMOVAL OF AMMONIA BY CARBONACEOUS ZEOLITE

The existence of the process in the second of these equations is confirmed by the fact that in many distribution systems nitrites can be found, although the raw water contains only ammonia. Calculations from energy relations show that the energy in the ammonia in a million gallons of the University of Illinois water supply would be sufficient to produce 40 pounds of bacterial growth (dry weight). This material would yield 800 pounds of wet sludge of 95 per cent moisture content and contains only about 12 per cent of the nitrogen of the ammonia in the original water. Even if we do not anticipate that the biological reaction uses all the ammonia available, we can nevertheless assume that the ammonia will furnish energy and nitrogen for a great amount of organic sludge. Elimination of the ammonia from the distribution system will therefore help to reduce considerably the after-growth in pipe lines.

Elimination of Ammonia

It was first thought that the ammonia could be eliminated by the formation of ammonium magnesium phosphate. To study this possibility, two series of experiments were run on 5-liter samples with trisodium phosphate as the source of phosphate ions. Since trisodium phosphate is also used as a water softener, lime was employed to soften the water and to aid the phosphate to react with the ammonia. Neither the trisodium phosphate nor the lime alone had any effect on the ammonia. Even if the trisodium phosphate and lime were introduced at practically the same time, no effect on the ammonium content could be found within experimental error (actual reduction from 1.6 to 1.52 p. p. m. ammonia nitrogen). If the lime was introduced first and, after 20 minutes of reaction time for the lime softening, twice the necessary amount of trisodium phosphate was added to bind the ammonia, a slight reduction of the ammonia from 2.0 to 1.3 p. p. m. was found as the best result. Apparently trisodium phosphate reacts too easily with calcium to be effective for the removal of ammonia.

The recent development of carbonaceous zeolites offers a possibility for the removal of ammonia. Whereas ordinary silica zeolites have the property of base exchange (that is, they replace calcium and magnesium ions in the water by sodium ions), carbonaceous zeolites have the property of hydrogen-ion exchange. They are able to replace any metallic ion by hydrogen ions and thus form acids in the treated water. Ammonia is included in the ions that are removed by carbonaceous zeolites.

Tests were made with the tap water of the University of Illinois. This water is aerated and filtered to remove iron and then chlorinated. It is practically a pure carbonate water, free of sulfates, but after heavy chlorination it contains about 5 p. p. m. chlorine ions. On an average, the water contains the following metallic ions in parts per million: calcium, 60.6; magnesium, 28.2; sodium, 56.5; ammonium, 2.7. In a long run the carbonaceous zeolite (Zeo-Karb, provided by the Permutit Company) shows two cycles with this type of water: first an acid cycle in which all metallic ions are removed, then a sodium cycle in which the carbonaceous zeolite acts as a normal zeolite, removes only the hardness producing metals, and replaces them with the sodium extracted during the acid cycle. The boundaries between the cycles are not sharp, and there is somewhat a gradual change from one action to the other. This can also be found relative to the removal of ammonia.

In the acid cycle practically all the ammonia is removed. In the effluent an average is found of only 4.4 per cent of the ammonia in the raw water. At the end of the acid cycle, when the total solids increase, the ammonia content increases also to an average of 13.2 per cent of that in the raw water. During the sodium cycle very little ammonia is removed, the effluent containing on an average 77.8 per cent of that of the raw water. At the end of the sodium cycle as soon as the hardness increases, the carbonaceous zeolite seems to be unable to retain the ammonia; at least an increase in ammonia was found then, the content of the effluent averaging 120 per cent of that of the raw water.

Carbonaceous zeolites, if regenerated with sodium chloride, act like siliceous zeolite in removing the hardness from the water. Probably in this case they will also remove ammonia during the sodium cycle, at least at the beginning of the cycle. But to obtain full benefit of the special properties of the carbonaceous zeolites they should be used only in the acid cycle—i. e., after regeneration with an acid. It is during this acid cycle that the carbonaceous zeolites form an excellent and reliable means for reducing the ammonia content of the water to a very low amount, averaging in these tests 0.12 p. p. m.

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Aerodynamics of Trickling Filters

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During the past decade cities and industries have been forced more and more, because of social and economic pressures, to treat their waste waters. Unfortunately, adequate disposal systems are being installed very slowly because the methods of treatment now employed are extremely costly and place a heavy burden on the taxpayers or concerns involved. There is, therefore, a need for more basic research to ensure the further development of the various methods of treatment.

This paper is concerned with the flow of air in low-capacity filters and particularly in the more recently developed continuous high-capacity trickling filters. During continuous distribution of water the rate of air flow is independent of the dosage up to 20 million gallons and is found to be a straight-line function of the difference in air and water temperatures. Pulsations in air flow during intermittent dosage may be explained on the basis of increased heat transfer during the distribution period.

MOST engineers recognize that adequate ventilation is essential for the proper operation of the trickling filters employed in sewage treatment. However, there is wide disagreement as to the manner and mechanism by which the flows of air take place. Some say the flow may be upward or downward through the filter, and others state that it is always downward. It is generally agreed, however, that ventilation is essential, and that if it is not adequate, decreased efficiency (*11*) and possibly clogging of the interstices with biological flora (*8*) will result. Some authorities, however, regard ventilation as relatively unimportant (*7*).

During the course of the experimental work which led to the development of the high-capacity trickling filter by Halvorson at the University of Minnesota, it was noted that the flow of air was important to its operation (*5*). The influence of sewage and air temperatures, of humidification, and of the dragging effect of the water were difficult if not impossible to follow under the usual outdoor plant conditions because of the practical difficulties met in suitably controlling the experimental conditions. In this investigation an attempt was made to develop a more fundamental understanding of the mechanism of the flow of air by studying the influences of the above factors in a clean filter.

A viewpoint common among engineers is that the necessary air is carried down into the interstices of the rock by the descending flow of sewage water as a result of a dragging effect of the water on the air (*9*). Many consulting engineers feel that intermittent dosage of the sewage on the filter beds is essential in order to cause atmospheric oxygen to come in contact with the bacterial film; however, the successful operation of continuous high-capacity filters have shown that intermittent dosage is not necessary (*5*). It has been demonstrated that bottom ventilation is essential; otherwise the filter soon clogs because of the accumulation of excessive organic matter in the filter bed (*8*). Clogging (i. e., ponding), seems to occur most frequently in the fall and spring of the year, but little is known about the mechanism of this process. The tendency of trickling filters to clog, whether as a result of insufficient aeration or some other cause, has always been an important limiting factor to be considered in the design and operation of filters. Certain writers, however, have pointed out the desirability of uniform air on sewage flow and even advocated forced ventilation (*10*, *11*). Filters made of very fine particles (sand, cinders, etc.) give high reductions but are easily clogged, and have therefore been abandoned by engineers in favor of rock filters which can operate successfully at higher capacities and still give sufficiently high reductions of B. O. D. At present it is customary to use filters 6 to 8 feet deep, made of graded rock 0.75 to 3 inches in size, dosed at rates varying from a half up to a maximum of 4 million gallons per acre per day with a sewage B. O. D. between 200 and 500. This amounts to an average of only 0.066 to 0.52 pound of sewage water per square foot of filter surface per minute. The high-capacity filter, on the other hand, operates continuously at 20 to 25 million gallons per acre per day (m. g. a. d.) with excellent purification.

The flow of air through continuous high-capacity filters was found by Halvorson to be upward or downward, depending on the relative temperatures of the water and the outside air. In summer when the water was colder than the air, the flow was downward through the bed; in winter, the water was warmer and the flow of air upward. In the spring and fall when the air and water temperatures were about equal, there was very little air flow. A filter using forced draft at these times operated more successfully than one using natural draft (*6*). These observations were made by means of smoke drifts on the surface of the bed or in the outlet pipes. However, the highly variable and uncontrollable conditions affecting the outdoor experimental plant prevented the taking of even roughly quantitative measurements with any certainty of their significance, and the apparatus shown in Figure 1 was built for experimental purposes. It was proposed in this apparatus to make a fundamental investigation of several of the factors determining the flow of air in trickling filters. This was done by using pure water in place of sewage in order to eliminate unknown variables that would be encountered by a changing flora. Once the factors affecting air flow in a clean filter are known and measured, it will become possible to interpret their effect upon a filter treating sewage.

Factors Causing Air Flow in a Trickling Filter

A difference of air temperature inside and outside a filter bed will set up columns of air of different densities above the drainage system and result in a flow of air to the area of low pressure. If the air is cooled by the liquid in the filter, as is generally true during the summer months, its density will be increased and it will tend to flow downward. If the air is warmed in the bed, it will tend to rise through the stones and draw air from the bottom. The magnitude of the draft—that is, the pressure difference—causing this flow will depend on the difference of density of the columns of air above the drainage system and on the depth of the bed. The draft pressure, P, causing a vertical flow of air to take place can be calculated from the equation:

$$P = h\,(d_2 - d_1)$$

where h = depth of filter
d_1, d_2 = average air densities inside and outside the filter

The resulting air velocity will depend upon the resistance of the filter. By assuming certain temperature differences and using equations for the pressure drop through packed columns, estimates were made of the velocities to be expected and the apparatus was designed on the basis of these.

The reactions taking place in a biological filter give off a certain amount of heat, and, if this heat is sufficient to cause an appreciable rise in temperature, a flow of air will result from decreased air density. As a crude approximation of this effect one can choose a B. O. D. reduction through the filter itself of 100 and assume that this corresponds to about the same weight of organic matter in p. p. m. This can hypothetically be converted into gas with a heating value of about 600 B. t. u. per cubic foot. Then, per pound of water, it is not likely that more than $0.0001 \times 600/0.03$ or 2 B. t. u. are generated in the filter. Since the temperature of the filter is controlled by the temperature of the water, this heat will go mostly to the water and thus might raise its temperature 2° F. Because this is a lesser temperature effect in comparison to the usual outdoor and water temperature variations, it is not unsafe to say that probably the heat of reaction has little effect on the flow of air in a trickling filter.

As air comes in contact with the moist surfaces in the filter, its humidity will tend to increase, and since moist air is lighter

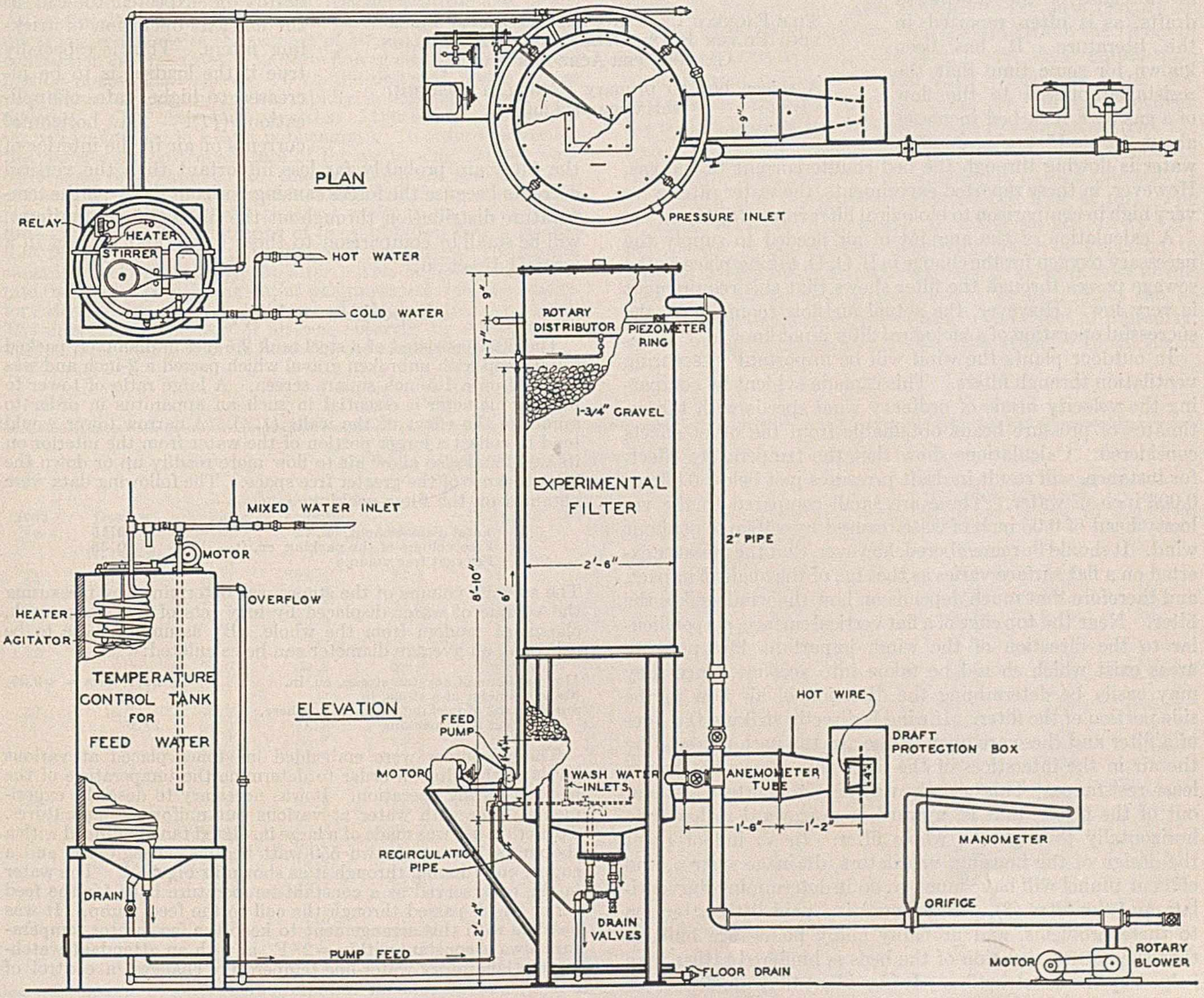

FIGURE 1. ASSEMBLY PLAN OF EXPERIMENTAL TRICKLING FILTER

than dry air, an upward draft will result. A calculation of the possible draft pressures which can result from humidification of the air shows that the effect of humidity is only relatively important when the temperature of the air and water are about the same. The degree of humidification will increase with fine particles because of the larger area exposed and the greater resistance of fine filters to air flow.

Tile Packing Used in a High-Capacity Trickling Filter Plant Operating at 20 Million Gallons per Acre per Day

A screen but no primary settling is used with this open packing

It is commonly stated that the sewage water, in trickling through the rock, mechanically pulls the air along with itself and thus causes a downward draft. In a filter which is nearly filled with organic matter so that there is little free space and the displacement volume of the water itself becomes larger by comparison, some slight effect is possible but it is doubtful that this mechanical action is the cause of the downward drafts, as is often reported in the literature. It has been known for some time that the resistance offered to the flow of a gas by a rock bed increases about 10 to 15 per cent when water is flowing through the bed countercurrent to the gas. However, in these reported experiments, the water rates were very high in comparison to biological filter rates (*12, 13*).

A calculation of the amount of air needed to supply the necessary oxygen for the change in B. O. D. taking place as the sewage passes through the filter shows that this requirement is very low. However, the actual air flow required for the successful operation of a biological filter is not known.

In outdoor plants the wind will be important in securing ventilation through filters. This is made evident by comparing the velocity heads of ordinary wind speeds with the estimates of pressure heads obtainable from the other effects considered. Calculations show that the temperature effect, for instance, will result in draft pressures just below 0.002 or 0.003 inch of water. These are small compared to the velocity head of 0.05 inch of water caused by a 10 mile per hour wind. It should be remembered, however, that the pressure exerted on a flat surface varies as the sine of the angle of impact, and therefore that much depends on how the wind strikes the filter. Near the top edge of a flat vertical surface, perpendicular to the direction of the wind, important low pressure areas exist which should be taken into account, since they may easily be determining the direction of air flow in the side portion of the filter. If wind is directly striking the sides of a filter and these are open to the air, the path followed by the air in the interstices of the filter will always be that of least resistance. This usually will be the shortest distance out of the filter—that is, upward or downward rather than horizontally through the whole filter. In an indoor plant the design of the housing, ventilators, drainage system, and effluent tunnel will have much to do in determining the ventilation of the filter (*3*). Engineers have paid little attention to these problems, and probably many plants are built so that the natural aeration of the beds is hindered rather than helped by the construction. It is evident that the flow of air in a filter will always follow the path of least resistance in accordance with the pressure gradients; if, for instance, the drainage system is such a poor one that it offers a real resistance to air flow, it is only logical that in some cases the flow of air may actually be downward in one section of the filter and upward through another section where for one reason or another the resistance to air flow is low. The net effect of this condition is nonuniform and reduced air flow in all parts of the filter, with the presence of stagnant air sections in some parts of the bed. At the low rates (1 or 2 m. g. a. d.) still being used, probably sufficient air for these low dosages is obtained in most of the filters so that clogging has not always been the result. Nevertheless, such conditions are indications of poor distribution and poor design, which can hardly be expected to lead to the efficient operation of trickling filters. This is especially true if the loading is to be increased to higher rates of application (*11*). The horizontal currents of air in the interior of the filter are probably far less important than the vertical currents because the forces causing horizontal flow, if the temperature distribution throughout the filter is fairly uniform, will be small in comparison to those forces and will act in a vertical direction.

Experimental Apparatus

The filter consisted of a steel tank 2.5 feet in diameter, packed 6 feet deep with unbroken gravel which passed a 2-inch and was retained on a 1.5-inch square screen. A large ratio of tower to particle diameter is essential in such an apparatus in order to minimize the effect of the walls (*1, 4*). A narrow tower would tend to collect a larger portion of the water from the interior on its walls and also allow air to flow more readily up or down the sides because of the greater free space. The following data were obtained on the filter packing:

Total displacement, cu. ft.	29.15
Free volume of the packing, cu. ft.	10.38
Per cent free volume	35.6

The average volume of the stones was determined by measuring the volume of water displaced by fifty sets of ten stones each, chosen at random from the whole. By assuming these to be spherical, an average diameter can be calculated:

Mean volume of any ten stones, cu. in.	24.7 ($\sigma m = \pm 0.25$)
Mean diameter of a stone, in.	1.68
Surface area of packing calcd. as a sphere, sq. ft./cu. ft. of packing	27.6

Thermocouples were embedded in stones placed at various levels of the filter in order to determine the temperature of the packing during operation. It was necessary to dose the experimental filter with water at various but uniform temperatures. To do this, use was made of a large insulated tank equipped with a thermostatic control, two 550-watt heaters, an agitator, and a copper coil running through it as shown in Figure 1. The water in the tank served as a constant-temperature bath for the feed water which passed through the coil to the feed pump. It was possible with this arrangement to keep the feed water temperature always constant within ±2° F., or with an attendant watching the laboratory water-line temperature changes, a control of 0.2° F. was not difficult to maintain.

Water was supplied to the apparatus from the temperature control tank by the gear pump installed as shown in Figure 1. By changing pulleys and using a speed reducer, it was possible to dose the bed at constant rates varying from 1 to 30 or more m. g. a. d. This was determined by weighing the water draining from the filter in a measured time. The pump delivery was very constant during the course of any one experiment. The temperature of the water distributed was determined by means of a thermometer fixed in the feed line just ahead of the distributor. The outlet water temperature was determined by taking the temperature of the water as it drained out of the tank through the siphon arrangement shown in Figure 1. The siphon served to prevent air from escaping except past the heated wire in the contracting tube. In order to decrease heat transfer to or from the room, the base of the tank had been thickly coated with wax. No difficulty was experienced in duplicating either water temperature reading.

The temperature of the air outside the tank was taken from thermometers placed near the tank, at levels 4.5 and 7.5 feet above the floor. Air flow readings were taken only when room temperatures had been constant for some time. The laboratory temperatures varied enough however to make a 0.1° C. calibration of the 0–100° C. thermometers sufficiently accurate for the data. Air humidity readings were taken with a sling psychometer. Small rotary distributors, which caused no appreciable air disturbance, were designed. They rotated at about 60 r. p. m. and dosed the filter with the water so that no stone on the surface layer of the packing was not wetted. The distribution was tested by measuring the volumes collected in 250-cc. beakers placed on the rock. These were practically the same no matter where the beakers were placed.

In order to measure the very low movements of air which take place through the filter, it was necessary in the first place to develop an instrument which would be sufficiently sensitive and at the same time offer no appreciable resistance to the flow of air. An electrically heated platinum wire placed in a contracting tube offers low resistance to the passage of air; at the same time the contraction ensures a steady uniform flow of air past the wire over a wide range of air speeds. With the designed bridge it was possible to take measurements rapidly in succession with little difficulty. (The design and operation of this hot wire anemometer will be detailed in a later publication.) In order to allow for the changes in the temperature of the air passing the hot wire, corrections were applied to the milliammeter reading. The anemometer was calibrated satisfactorily, and the instrument was found, during the later experimental work, to be well adopted to the purpose. The scattering of the calibration data indicated that the maximum error in reading was ±1.2 inches per minute superficial velocity through the filter. This is sufficiently accurate for the purpose. The outlet was protected from the laboratory drafts with an open box around which cloths were hung. The direction of the flow of air was observed by following the drift of ammonium chloride fumes in the contracting tube.

Continuous Dosage

In these experiments the filter was continuously dosed with water at constant temperature, and no air flow measurements were accepted until the temperature of the outlet water had become substantially constant. At the lower distribution rates the filter was dosed at least 15 hours before readings were taken, and a single run was sometimes carried on for 2 days to ensure steady conditions of temperature. The room temperature was held as nearly the same as possible for some time before an anemometer reading was recorded so that the data given could be accepted as being taken at, or at least quite near, equilibrium conditions of temperature and air flow. It took a long time for changes in water temperature to affect the air flow; however, changes in air temperature were within a few minutes followed by air velocity adjustments to a steady value. This is partly due to the fact that the air has only a slight heating or cooling effect on either the water or the filter bed itself.

Data were taken at various water and air temperatures and also at various water distribution rates in order to determine the effect of these variables on the flow of air. The data are given in Table I. The rates were varied between the limits of 1 and 20 m. g. a. d. since these include the usual dosage rates of both low- and high-rate trickling filters.

If the difference of the arithmetical averages of the temperature of the air outside the filter and of the water passing through the bed is plotted against the measured air velocity, a straight line can be drawn through all the data (Figure 2).

The following conclusions may be drawn for the range of conditions investigated: The flow of air under equilibrium conditions of temperature and with continuous water distribution is a straight-line function of the difference between the temperature of the outside air and the temperature of the water. Since the points fall on the same line, independent of the dosage rates, evidently an increase in dosage rate from 1 to 20 m. g. a. d. has no large effect on the flow of air. The dragging effect of the descending water on the air is very small since, if appreciable, this effect could be expected to increase with dosage rate and therefore to cause greater downward flows as the rate is increased. No such effect can be observed from the plot of the data. The effect of humidity, which tends to cause an upward flow because moist air is

TABLE I. AIR FLOW AT EQUILIBRIUM (DOSAGE CONTINUOUS)

Run No.	Dosage Rate	Water Temp.			Room Air Temp.					Temp. Difference of Air and Water	Air Flow	
		Entering filter	Leaving filter	Average	Upper thermometer	Lower thermometer	Average	Air Passing Anemometer	Room Humidity		Per sq. ft. of area per min.	Direction of flow
	M. g. a. d.	° *F.*	° *F.*	° *F.*	° *F.*	° *F.*	° *F.*	° *F.*	%	° *F.*	*Cu. ft.*	
11	20.5	75.2	75.9	75.5	77.0	76.8	76.9	76.5	28	1.4	0.35	Up
		75.2	76.3	75.7	77.0	76.8	76.9	75.9		1.3	0.30	Up
		75.2	76.3	75.7	77.0	76.5	76.7	75.9		1.3	0.30	Up
		74.7	75.6	75.1	76.8	76.5	76.6	75.7		1.5	0.28	Up
12	20.0	59.2	63.1	61.2	81.3	78.4	79.9	71.6	52	18.7	2.11	Down
		59.0	60.8	59.9	80.4	78.1	79.2	71.1		19.3	2.19	Down
		60.3	61.2	60.7	82.2	81.9	82.0	72.9		21.3	2.35	Down
13	16.2	64.2	66.0	65.1	80.6	79.2	79.9	74.3	35	14.8	1.60	Down
		64.9	65.8	65.4	82.8	81.3	82.0	74.3		16.6	1.77	Down
		65.8	66.7	66.3	83.5	82.1	82.8	75.2		16.5	1.72	Down
		66.9	67.5	67.2	81.9	80.9	81.4	75.2		14.2	1.46	Down
		65.3	65.8	65.5	77.9	77.4	77.6	73.4		12.1	1.30	Down
14	8.7	65.7	68.5	67.1	82.8	81.1	82.0	75.7	26	14.9	1.52	Down
		67.5	68.9	68.2	83.7	81.8	82.8	76.7		14.6	1.52	Down
		69.1	69.3	69.2	83.7	82.1	82.9	76.8		13.7	1.46	Down
		68.2	69.6	68.9	79.9	76.2	78.1	73.6		9.2	0.85	Down
		69.4	70.0	69.6	80.1	77.0	78.6	75.0		9.0	0.85	Down
		71.1	72.5	71.8	82.9	81.2	82.0	78.1		10.2	1.00	Down
		..	72.5	71.8	82.9	80.9	81.9	78.1	24	10.2	0.97	Down
15	1.0	66.8	67.3	67.1	73.8	71.4	72.6	70.3	26	5.5	0.28	Down
		67.1	70.5	68.8	77.4	74.7	76.1	73.6		7.3	0.55	Down
16	2.3	65.7	71.2	68.4	82.9	80.8	81.9	75.7		13.5	1.38	Down

lighter than dry air, explains the fact that the line of the data does not pass through the origin. The extent of this displacement is a measure of the effect of humidity under the experimental conditions. Some approximate measurements showed that the change in humidity of the air while passing through the filter is not large. The temperature of the packing was also determined during the course of a high rate experiment. These measurements showed the stones to be at the temperature of the water and not at that of the air. On stopping the water distribution when equilibrium had been reached, there was little or no change in air velocity for some time; this was due to the relatively small heating or cooling effect of the air on the filter temperature.

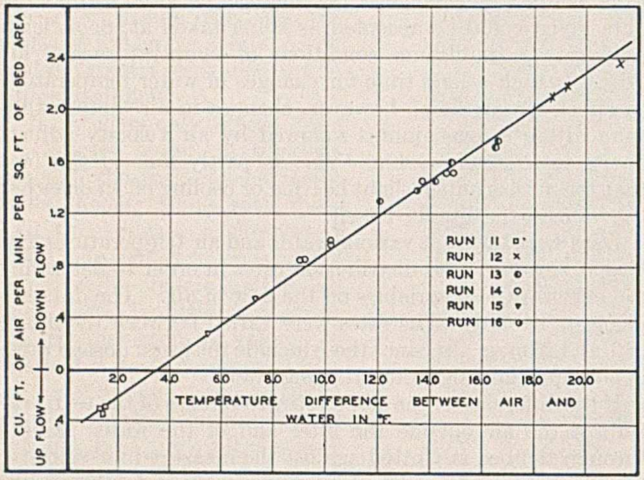

Figure 2. Relation between Flow of Air through the Experimental Filter and Temperature Difference between Air and Water

Intermittent Dosage

Since most trickling filters are still operating at low rates of 1 or 2 m. g. a. d. and are using intermittent dosage, it is worth while to show how the flow of air takes place in them during the short periods of operation and the long "rest" periods.

Before beginning the intermittent dosage experiment, the filter was dosed continuously for 12 hours at 20 m. g. a. d. with water at 75–77° F. (about room temperature) to obtain a uniform temperature throughout the filter. The filter was then dosed intermittently with cold water at an average daily rate of 2.1 m. g. a. d. For 2 minutes water at 60.8° F. was distributed on the filter at a rate of 26 m. g. a. d. This was followed by a 23-minute rest period. This intermittent distribution was continued for ten cycles; during this time frequent anemometer and air and water temperature readings were taken. The air flow measurements during the dosage periods were taken about every 30 seconds in order to follow the rapid changes. Finally the filter was dosed continuously at 26 m. g. a. d. until the flow of air had become nearly steady. The plot of the results of this experiment is shown in the upper half of Figure 3. The humidity of the room was close to 30 per cent throughout this experiment.

During intermittent dosage the pulsations in air flow are due to increased heat transfer during the distribution period and may be explained as follows: Before intermittent dosage was started, the filter was at a uniform temperature throughout, which was due to the previous continuous dosage at 20 m. g. a. d. Because of the effect of humidity and some temperature difference between the packing and the room air, an upward draft of 0.62 cubic foot per square foot per minute was taking place through the bed. Cold water at 60.8° F. was then distributed over the packing for 2 minutes. As it flowed through, this water cooled the air in the filter enough to set up a downward draft pressure which was sufficient to equalize the already present upward draft forces so that, during the first dosing period, the actual flow was practically zero; at the same time heat transfer was taking place from the rock to the water, and the temperature of the packing, especially near the top of the filter, was somewhat lowered. This was shown by the rise in temperature of the outlet water, which was far too large a rise to be accounted for by the heat coming from the air. Since the average temperature of the filter was being lowered by each application of cold water, the upward draft was lowered during each succeeding rest period, and after the eighth cycle, the direction of air flow was always downward through the filter. If the cycles were continued, the downward flow through the bed would continue to decrease until the equilibrium flow had been reached. This was not practical experimentally because it was impossible to keep the large laboratory at constant temperature for a sufficiently long period (probably, judging from the slope of the curves, over 10 hours would be needed). The minor rise in air flow noted during each resting period was probably the result of slow heat transfer from the interior of the stones to their wet, colder surfaces.

After the second cycle, the cooling of the air in the filter, which took place during the period of distribution, was sufficient to cause a downward air flow during the dosing period. The downward draft became more important with each succeeding dose of cold water because the stones were becoming colder. Continuous dosage at 26 m. g. a. d., following the tenth cycle, cooled the filter rapidly so that equilibrium was practically reached in one hour, as the upper part of Figure 3

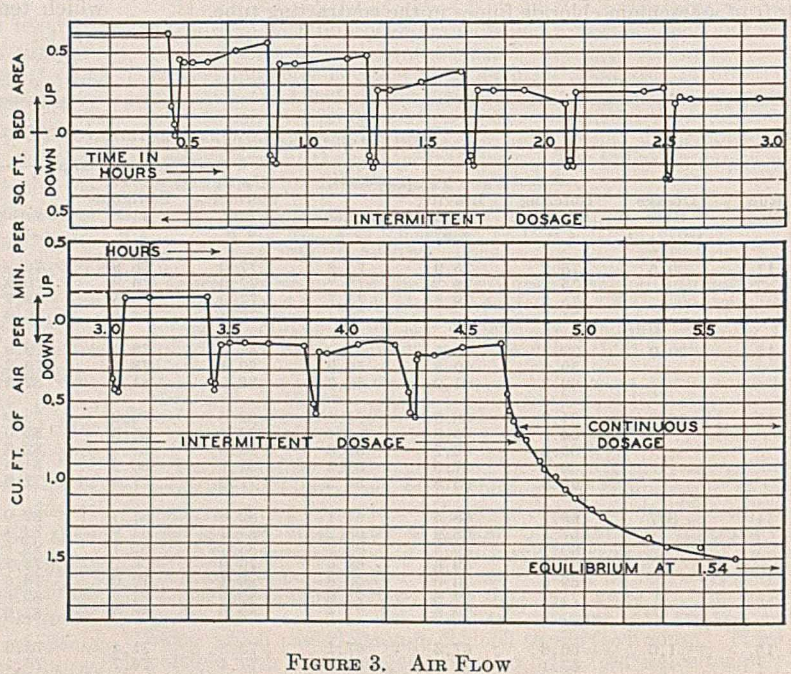

Figure 3. Air Flow

(*Above*) Intermittent dosage; average rate, 2.1; momentary rate, 26.0 m. g. a. d.
(*Below*) Intermittent dosage at low rate, continuous dosage at high rate

Table II. Air Flow during Intermittent Dosage

		Water Temp.			Room Air Temp.					Air Flow	
Momentary Dosage Rate M. g. a. d.	Time Hr.:min.:sec.	Entering filter ° F.	Leaving filter ° F.	Average ° F.	Upper thermometer ° F.	Lower thermometer ° F.	Average ° F.	Air Passing Anemometer ° F.	Temp. Difference of Air and Water ° F.	Per sq. ft. of area per min. Cu. ft.	Direction of flow
0	0:00:00	Bed resting and at about the same temperature as the room									
0	0:24:00	..	..	..	75.4	73.9	74.5	74.5	...	0.61	Up
26	0:25:00	..	..	..	..	..	..	..	...	..	...
26	0:25:30	..	..	..	..	..	..	..	...	0.16	Up
26	0:25:50	..	..	..	..	..	..	..	...	0.04	Up
26	0:26:10	..	..	..	..	..	..	..	...	0.00	...
26	0:26:40	60.8	72.0	66.4	75.2	73.8	74.5	75.2	81.	0.02	Down
26	0:27:00	..	..	..	..	..	..	..	...	0.02	Down
0	0:27:30	..	..	..	..	..	..	..	...	0.37	Up
0	0:28:00	..	..	..	..	..	..	..	...	0.45	Up
0	0:29:00	..	..	..	..	..	..	..	...	0.43	Up
0	0:31:00	..	..	..	..	..	..	..	...	0.43	Up
0	0:35:00	..	..	..	..	..	..	..	...	0.45	Up
0	0:43:00	..	..	..	74.5	73.8	74.1	..	...	0.51	Up
0	0:49:00	..	..	..	75.0	73.6	74.3	74.8	...	..	...
26	0:50:00	..	..	..	..	..	..	..	...	..	...
26	0:50:30	..	..	..	..	..	..	..	...	0.14	Down
26	0:51:00	..	..	..	..	..	..	..	...	0.16	Down
26	0:51:30	..	..	..	..	..	..	..	...	0.16	Down
26	0:52:00	61.3	73.6	67.5	75.2	73.8	74.5	74.8	7.0	0.18	Down
0	0:53:00	..	..	..	..	..	..	..	...	0.42	Up
0	0:57:00	..	..	..	..	..	..	..	...	0.42	Up
−0	1:04:00	..	..	..	..	..	..	..	...	0.42	Up
0	1:10:00	..	..	..	..	..	..	..	...	0.46	Up
0	1:14:00	..	..	..	74.7	73.6	74.1	75.4	...	..	...
26	1:15:00	..	..	..	..	..	..	..	...	..	...
26	1:15:30	..	..	..	..	..	..	..	...	0.16	Down
26	1:16:00	..	..	..	..	..	..	..	...	0.20	Down
26	1:16:30	60.6	73.8	67.2	75.0	73.6	74.8	..	7.6	0.23	Down
26	1:17:00	..	..	..	..	..	..	..	...	0.20	Down
0	1:18:00	..	..	..	..	..	..	..	...	0.26	Up
0	1:21:00	..	..	..	..	..	..	..	...	0.26	Up
0	1:29:00	..	..	..	..	..	..	..	...	0.31	Up
0	1:39:00	..	..	..	74.8	73.4	74.1	75.7	...	0.37	Up
Data of Six Following Distribution Periods Are Plotted in Figure 3											
0	4:14:00	60.8	73.4	67.1	73.9	72.5	73.2	73.8	6.1	0.16	Down
26	4:15:00	..	..	..	..	..	..	..	...	..	...
26	4:15:30	..	..	..	..	..	..	..	...	0.46	Down
26	4:16:00	..	..	..	..	..	..	..	...	0.58	Down
26	4:16:30	..	..	..	..	..	..	..	...	0.58	Down
26	4:17:00	..	..	..	..	..	..	..	...	0.62	Down
0	4:17:30	..	..	..	..	..	..	..	...	0.26	Down
0	4:18:00	..	..	..	..	..	..	..	...	0.22	Down
0	4:19:00	..	..	..	..	..	..	..	...	0.23	Down
0	4:20:00	..	..	..	..	..	..	..	...	0.22	Down
0	4:23:00	..	..	..	..	..	..	..	...	0.22	Down
0	4:29:00	..	..	..	..	..	..	..	...	0.17	Down
0	4:39:00	60.4	73.4	66.9	73.8	72.2	73.0	..	...	..	...
26	4:40:00	..	..	..	..	..	..	..	...	..	...
26	4:40:30	..	..	..	..	..	..	..	...	0.47	Down
26	4:43:00	..	..	..	73.8	72.1	73.0	73.4	...	0.73	Down
26	4:45:00	60.3	71.4	65.8	..	..	..	..	7.2	0.76	Down
26	4:48:30	..	..	..	..	..	..	..	...	0.90	Down
26	4:52:30	60.3	70.3	65.3	73.8	72.3	73.0	..	7.7	1.00	Down
26	4:55:00	..	..	..	..	..	..	..	...	1.08	Down
26	4:57:30	..	68.9	..	..	..	..	71.6	...	1.14	Down
26	5:01:30	..	..	..	..	..	..	..	...	1.20	Down
26	5:04:30	60.3	67.3	63.7	73.9	72.3	73.2	71.1	9.5	1.26	Down
26	5:29:30	60.3	63.7	61.9	74.1	72.3	73.2	68.7	11.3	1.44	Down
26	5:41:30	60.3	62.4	61.3	73.6	72.1	72.8	68.8	11.5	..	Down
26	5:57:30	59.9	60.8	60.3	73.0	71.6	72.3	66.7	12.0	1.47	Down
26	6:17:30	69.5	60.4	59.9	72.9	71.4	72.1	66.2	12.2	1.54	Down
26	6:37:30	69.7	60.3	60.1	72.7	71.4	72.1	66.2	12.0	1.54	Down

shows. The equilibrium value is somewhat higher than those indicated by Figure 1, which is based on data taken up to 20 m. g. a. d. However, the value 1.54 cubic feet per square foot per minute is entirely in accord with other data taken at higher rates than 20 m. g. a. d.

On the basis of this experiment the following conclusions may be made: The pulsations observed in the filter during the dosing periods are not due to a dragging effect of the descending water on the air in the filter. When dosed intermittently, the temperature of a filter slowly tends to approach that of the water distributed. During intermittent operation of a filter, rapid pulsating changes in air flow take place during the dosage period if the temperature of the filter is not the same as that of the water being distributed on it. These pulsations may be towards a lesser or a greater flow of air than that taking place during the rest period. This depends altogether upon the direction of flow during the rest period and whether the water temperature is tending to cause a reversal in air flow direction or not.

Our data would seem to indicate that, under the usual operating conditions, intermittent distribution will not bring as much air through the filter as continuous distribution. The lag in reaching the equilibrium air flow, as a result of the intermittent operation of the filter, will cause the total amount of air passing through to be less than that obtained during continuous operation.

Resistance to Air Flow

In a filter containing biological flora, the resistance to air flow can be expected to vary widely as the amount of organic matter on the stones changes. The filter may be almost clogged at times of poor operation and may be quite clean following a sloughing-off period. In any case, the resistance will always be greater than that of a clean filter. On the other hand, the pressure heads due to temperature and humidity effects may be expected to increase as a result of better heat transfer, etc., due to the more intimate contact of air and water in the smaller interstices of a loaded filter. But there are limits to the increased pressure head which can possibly be attained through these effects. In the natural draft experiments, the temperature of the outlet air was found to be about halfway between that of the inlet air and of the water. If the outlet air temperature in a filter of smaller packing or in one containing biological flora were to reach that of the water, the pressure head for a given difference of water and outside air temperature would be doubled. As a maximum condition, the air throughout the height of the tower would be at the temperature of the water, but even under these extreme conditions the pressure head has only been increased four times. It would take only a minor increase in the resistance of the filter due to the presence of biological flora to offset the higher pressure head gained by the better contact of the air and the filter. In other words, the forces causing a flow will increase but only slightly in comparison to the probable increase in resistance; as a result the actual velocities will always be lower than those observed in a clean filter.

The resistance of a filter increases rapidly as the size of the particles is decreased. From the equations of Chilton and Colburn we can deduce that if the flow is viscous, a reduction of stone size from 1.75 to 0.25 inch will increase the resistance to the passage of air $(1.75/0.25)^2$ or forty-nine times (*2*). The highest possible increase in pressure due to temperature, on the other hand, is only fourfold. Although advantages are to be gained in using smaller particle sizes because of the increased surface, it is evident that definite precautions must be taken if adequate air flow is to result in a fine filter. Unless this is done, the gain in area is obtained at the expense of a decrease in air flow which may be the more important factor for the successful operation of a filter.

Summary

1. The flow of air at equilibrium and with continuous water distribution is a straight-line function of the difference between the temperature of the outside air and the temperature of the water.

a. This relation is not appreciably affected by changes in water dosage rates between the limits of 1 to 20 m. g. a. d.

b. The effect of humidification of the air is relatively slight except when the temperature of the air and water is approximately the same. It will tend to cause a slight upward draft under those conditions.

2. The dragging effect of the descending water is negligible.

3. During intermittent distribution pulsations in air, flow will take place as a result of the increased heat transfer during the dosing period. For a given amount of water being dosed on a filter, the data indicate that intermittent dosage will not bring as much air through the filter as continuous dosage. The maximum air flows obtained during the pulsations in intermittent dosage are less than the equilibrium flow set up by continuous distribution.

4. The filter medium, during continuous dosage at high rates, comes to the temperature of the water and not to that of the air flowing in natural draft.

Literature Cited

(1) Baker, T., Chilton, T. H., and Vernon, H. C., *Trans. Am. Inst. Chem. Eng.*, 31, 296 (1935); Selheimer, C. W., Jr., *Chem. & Met. Eng.*, 41, 149 (1934); Baker, E. M., *Ibid.*, 41, 243 (1934).
(2) Chilton, T. H., and Colburn, A. F., IND. ENG. CHEM., 23, 913 (1931).
(3) Emsweler, J. E., and Randall, W. C., Univ. Mich., Dept. Eng. Research, *Bull.* 3 (1926).
(4) Furnas, C. E., U. S. Bur. Mines, *Bull.* 307 (1929).
(5) Halvorson, H. O., *Water Works & Sewerage*, 83, 307–13 (1936).
(6) Halvorson, H. O., Savage, G. M., and Piret, E. L., *Sewage Works J.*, 8, 888–903 (1936).
(7) Hatfield, W. D., *Ibid.*, 3, 175–87 (1931).
(8) Levine, Max, and Goresline, H. E., Iowa Eng. Expt. Sta., *Bull.* 116, (1934).
(9) Metcalf, L., and Eddy, H. P., "American Sewerage Practice", Vol. III, New York, McGraw-Hill Book Co., 1935.
(10) Phelps, E. B., "Principles of Public Health Engineering", New York, MacMillan Co., 1925.
(11) Pönninger, R., *Gesundh.-Ing.*, 61, 260–4 (1938).
(12) White, A. M., *Trans. Am. Inst. Chem. Engrs.*, 31, 391 (1935).
(13) Whitman and Keats, IND. ENG. CHEM., 14, 186 (1922).

Extraction of Saponin from Soap Nut

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SOAP nut (Figure 1) is the fruit of a handsome tree (Figure 2) found throughout India. Its two species are *Sapindus mukorossi* Gaerten, and *Sapindus laurifolius* Vahl. The former is found throughout northern India and grows in the lower hills up to an altitude of 4000 feet; the latter is found mostly in western, central, and southern India and Ceylon (*6*). The trees are called locally by the vernacular name, *Ritha.* Soap nut has been employed as a detergent from very ancient times and in certain cases, especially in washing woolen fabrics and silk, and in cleaning jewelry, it is given preference over soap and other cleansing agents. Some work has been done in the past to extract saponin from the nut, but the methods cannot be employed on a commercial scale. Asahina and Shimidzu (*1*) tried to prepare saponin from the alcoholic extract of soap nut pericarp by adding lead subacetate, removing the excess lead by hydrogen sulfide, acidifying at 40° C. with hydrochloric acid, and storing for several days; it is stated that saponin was then precipitated as white crystals. It was purified by being dissolved in alcohol and filtered through animal charcoal. As stated by the authors, saponin precipitated very slowly and with difficulty by this method. Besides, the method of purification is wasteful since animal charcoal retains much of the saponin. The authors did not state the percentage yield obtained. Basu (*2*) tried the different methods that are used for preparing saponin from important saponin-yielding plants but was unsuccessful in suggesting a practical method for extracting it from soap nut (*3*). In the present investigation

A method has been worked out for the extraction of saponin from soap nut, a raw material which is found abundantly in India. This method is efficient and is practicable commercially. The yield of saponin was 17.21 per cent of the weight of the nut. This is the highest so far obtained from any saponin-yielding plant.

an attempt has been made to develop an efficient method for the industrial extraction of saponin from soap nut.

Extraction

The soap nut selected was from the *Sapindus mukorossi* species. The nut consisted of 56.2 per cent pericarp and 43.8 per cent seed. Saponin is found in the pericarp. No attempt was made to determine the exact composition of the pericarp. Besides saponin, it is known to contain gums, resins, etc.

The following practical method for the extraction of saponin from soap nut was worked out:

The pericarp was dried in the sun and ground to a rough powder. The powder was refluxed with ethyl acetate for 3 to 5 hours. After allowing it to settle for some time ethyl acetate was drawn off. Three extractions with this solvent were sufficient to remove all the available saponin. The fractions of ethyl acetate extract were collected and subjected to distillation; ethyl acetate that passed over as distillate was collected and the residue left was removed. The residue is a pale yellow, viscous, semiplastic substance. It dried under a desiccator to a hard mass at room temperature. When powdered, this mass gave saponin that was almost creamy in color. For purification a concentrated aqueous solution was treated with a saturated solution of barium hydroxide. The precipitated barium salt of saponin was washed with barium hydroxide in which it is insoluble, suspended in dilute ethyl alcohol, and decomposed by carbon dioxide into barium carbonate and saponin. The saponin solution was evaporated, and saponin was dissolved in ethyl alcohol and obtained by evaporation. The saponin yield was 30.625 per cent on the weight of the pericarp or 17.21 per cent on the weight of the soap nut. This yield is higher than has been obtained from any other known saponin-yielding plant (*5*).

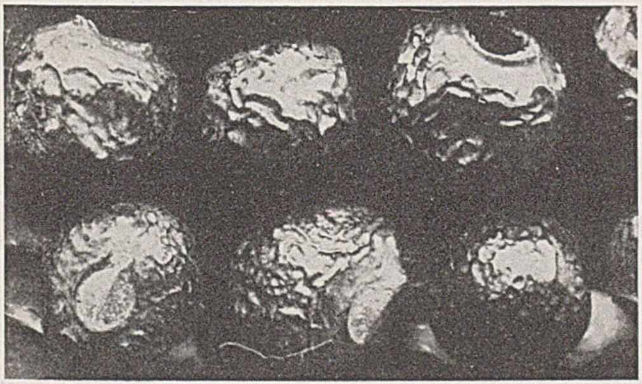

Figure 1. Soap Nuts

Properties and Uses

The saponin obtained was a white crystalline substance. It is insoluble in chloroform, benzene, sulfuric ether, and petroleum ether, but is soluble in methyl alcohol and water. It has no definite melting point but starts to fuse at 95° C. Its specific rotation $[\alpha]^{24}_{D}$ in ethyl alcohol is -15.5. With concentrated sulfuric acid it is reddish yellow in color which changes to violet on standing. With sulfuric acid and acetic anhydride it gives a deep red coloration. It is acidic in nature. When subjected to various methods of separation of the saponins from each other (*4*), it was found that no neutral saponin could be separated.

Elementary analysis showed the following results: carbon, 56.90 per cent; hydrogen, 8.26; oxygen 34.84. When hydrolyzed with 3 per cent sulfuric acid or, better still, with an alcoholic solution of hydrochloric acid, saponin gave crystallized sapogenin. The melting point of this sapogenin was 318–319° C. The other derivatives prepared were triacetyl and benzoyl. The melting point of the crude triacetyl derivative was 125–140° C., but it could not be crystallized from any solvent. The benzoyl derivative was crystallized from water. The melting point of the crude product was 105–107° C. and that of the crystallized product was 113–114° C.

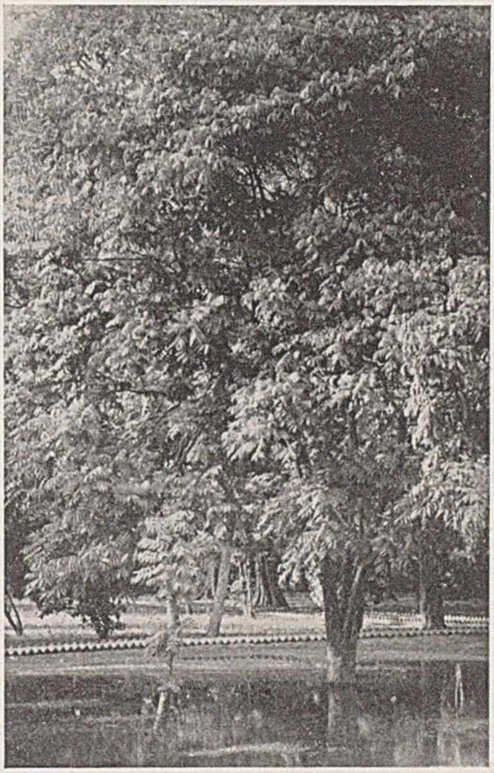

Figure 2. Soap Nut Tree

The soap-nut saponin prepared could be utilized for the same purposes as saponin from other sources—e. g., as an emulsifying agent for vegetable and essential oils, as a foam stabilizer, and in the manufacture of soapless shampoos.

Literature Cited

(1) Asahina and Shimidzu, *J. pharm. chim.*, [7] 14, 188 (1916).
(2) Basu, K., *Indian Soap J.*, 3, 9, 217 (1937).
(3) Kofler, Ludwig, "Die Saponine", Berlin, Julius Springer, 1927.
(4) Rosenthaler, L., and Ghosh, S., "Chemical Investigation of Plants", London, Bell & Sons, 1930.
(5) Thorpe, "Dictionary of Applied Chemistry", London, Longmans, Green & Co., 1922 and 1934.
(6) Watt, G., "Commercial Products of India", p. 979, London, John Murrey, 1908.

FROSTING OF VULCANIZED RUBBER

Frosting is a descriptive term for a particular type of dulling of the surface of vulcanized rubber articles, which occurs most frequently in warm, humid weather. Rubber vulcanized in a mold, in steam, or in air will frost, but the effect is most noticeable on the bright finish of air-cured products. Frosting is a microscopic disintegration of the surface caused by ozone in the air, and its action on the rubber is favored by warmth and humidity. Frosting can readily be reproduced in a laboratory test. It is prevented by protective films such as lacquer or varnish; by treatment after vulcanization with chlorine, bromine, or sulfur monochloride; or by incorporating in the rubber before vulcanization certain types of high-melting petroleum waxes or one of the antifrosting agents, of which p,p′-diaminodiphenylmethane is the most effective.

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RUBBER products, like most commodities today, must meet the public demand for attractive appearance. Anything which damages the finish is a problem for the technical man. An appearance problem which seems to have become frequent in recent years is concerned with a dulling or surface dimming of various types of rubber goods after vulcanization. This effect has been aptly called "frosting", and it sometimes resembles actual frost.

Frosting may be easily confused with bloom. It usually appears within a few hours or days after vulcanization. It differs from bloom in that it is not caused by migration to the surface of a constituent of the rubber composition. Bloom can usually be removed by solution in weak acid or alkali or in an organic solvent. Frosting cannot be removed. The microscopic appearance is also quite different.

Frosting may occur on rubber vulcanized in a press, or in an open-air or steam cure such as is used for footwear. It is most noticeable on the bright finish of air-cured rubber goods. Sometimes it appears almost immediately after removal from the vulcanizer as a bluish sheen which may later become almost gray. Frosting has been observed on a great variety of rubber products including footwear, raincoats, inner tubes, druggist's sundries, and other molded articles. Unfortunately there is no known way in which frosting can be removed after it has once formed. It can be covered with lacquer or other finish but this is seldom satisfactory when applied after vulcanization. A bloom of sulfur and sometimes of other materials can be removed by additional heating at vulcanizing temperatures, but this is not effective with frosting. If the rubber is not frosted within a few weeks after vulcanization, it seems to develop a resistance to frosting and is unlikely to frost later.

Frosting was determined to be due to the ozone in the air. So far as the writer knows, the cause was first determined by S. M. Boyd in 1931. He found that the effect could be reproduced by exposing vulcanized rubber without tension in warm, humid, ozonized air.

Frosting Test

A simple and rapid determination of the relative tendencies of different stocks to frost may be made by means of this test:

The equipment shown in Figure 1 consists of a chamber, roughly, 2 feet on each side, which is provided with an ozone generator for producing ozonized air. Suitable ozone generators may be purchased from manufacturers of this equipment or may be made by a design recently described (*5*). A moderate stream of dry air is passed through the ozone generator during the operation to ensure maximum efficiency. The ozonizer operates on the 110-volt a. c. lighting circuit. A 100-watt light bulb serves to heat the interior of the box.

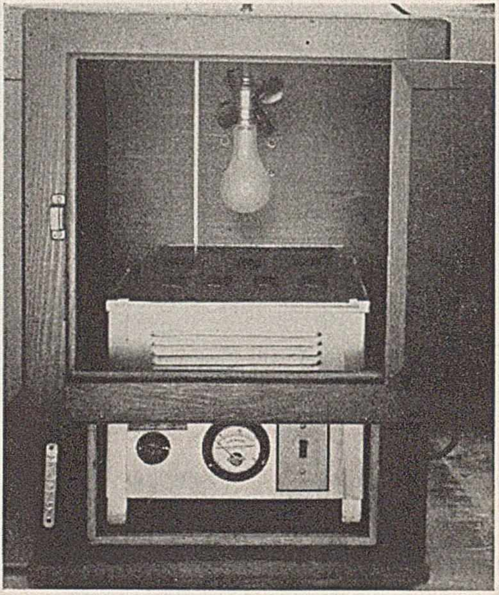


FIGURE 1. FROSTING TEST APPARATUS

In making the test, a sheet of blotting paper is saturated with water, laid flat on a glass plate placed in the box with the generator and light operating, and left for about one hour. The box should be tightly closed. The blotter is then thoroughly wet again, and the rubber samples to be tested are placed upon it. Care is taken that there is no water on the surface to be frosted. Under these conditions frosting is quite rapid. The time of exposure varies from a few minutes up to 3 hours, depending upon the nature of the stocks and upon the degree of frosting desired. Measurements show a temperature of 127° to 130° F. and a relative humidity of 70 to 75 per cent while the box is operating as described. Lowering the temperature and humidity slows the test, and if there is insufficient humidity, frosting will not take place.

Reaction of Ozone and Rubber

Frosting occurs almost exclusively in warm, humid weather. Apparently the activity of the ozone or the rubber is increased by moisture and warmer temperatures. Also under such weather conditions, windows are open and the outside air circulates a great deal more indoors than at other seasons.

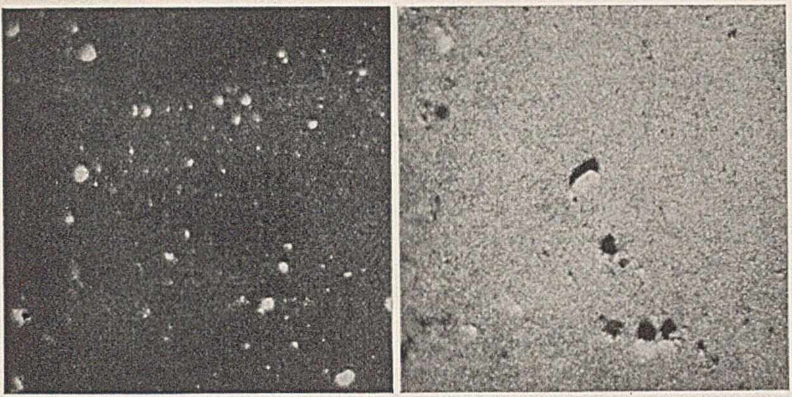


Figure 2. Unfrosted (*left*) and Frosted (*right*) Rubber Surfaces (×70)

Air is known to contain a minute amount of ozone, estimated by Reynolds (*4*) at 5 to 12 volumes per billion volumes of air. It is supposed to be formed in the upper atmosphere by ultraviolet light and reaches the lower atmosphere by diffusion and convection currents. The concentration is undoubtedly variable and tends to a maximum in the spring. An attempt was made to determine atmospheric ozone by the best chemical methods described (*1*) and with all possible precautions. The maximum amount found was 1.9×10^{-7} gram per liter of air or about 0.10 p. p. m. by volume of air. This determination was made in June and July, 1936.

Ozone was first shown by Williams (*8*) in 1926 to be the cause of the cracking of rubber under tension. This was further established by Van Rossem (*7*) who proposed the term "atmospheric cracking" to describe this effect.

Ozone attacks the double bonds of rubber to form an ozonide (*3*). The primary or secondary reaction product of ozone on rubber is a viscous liquid lacking in physical strength and therefore unable to withstand a stress. It appears that where ozone attacks stretched rubber it breaks, and thus relieves the tension in adjacent areas and decreases its reactivity to ozone. The strain is increased in the crack, and ozone continues to react at that point and cause the crack to grow. The surface strains in a piece of rubber are undoubtedly very nonuniform and result in a nonuniform reactivity to ozone.

It is not generally recognized that ozone will react with rubber which is not under tension. Harry L. Fisher found that a sample of unstressed pure gum stock in ozonized oxygen gained 0.2 per cent of its weight in 6 hours at room temperature. After the final weighing it was bent but showed no cracks, even under microscopic examination. Fisher also found that vulcanized rubber swollen by benzene cracked in ozonized oxygen; the strain produced by solvent absorption evidently had the same effect as tension. The action of ozone is not restricted to soft vulcanized rubber. Fisher found that bent samples of hard rubber, 0.5 mm. thick with a coefficient of vulcanization of 43, cracked in less than 2 minutes in ozonized oxygen.

Ozone Cracking and Frosting

Rubber behaves like a supercooled liquid with colloidal properties. Liquids exhibit surface tension, and this property is retained in supercooled liquids and solids (*6*) although it is not so easily demonstrated in the latter. Evidence of the surface tension of rubber is that the surface of unvulcanized rubber flows when its viscosity is reduced by heating. This seems to explain the glossy finish on air-cured rubber.

The surface of rubber is therefore under tension even though the mass of the rubber is not strained. The surface is thus reactive to ozone. When exposed to ozonized air, the surface is disintegrated into a maze of minute cracks. This microscopically cracked surface designated as frosting is distinguished from atmospheric cracking of stretched rubber principally in the size and number of the cracks.

The surface of vulcanized compounded rubber is essentially a continuous transparent film of rubber which transmits or reflects light without diffusion. The appearance and color of a pigmented rubber composition depend upon the selective absorption and reflection of light by the pigment dispersed in the rubber. Disintegration of the surface rubber film causes it to reflect diffused light directly, and the color of the underlying pigment is obscured.

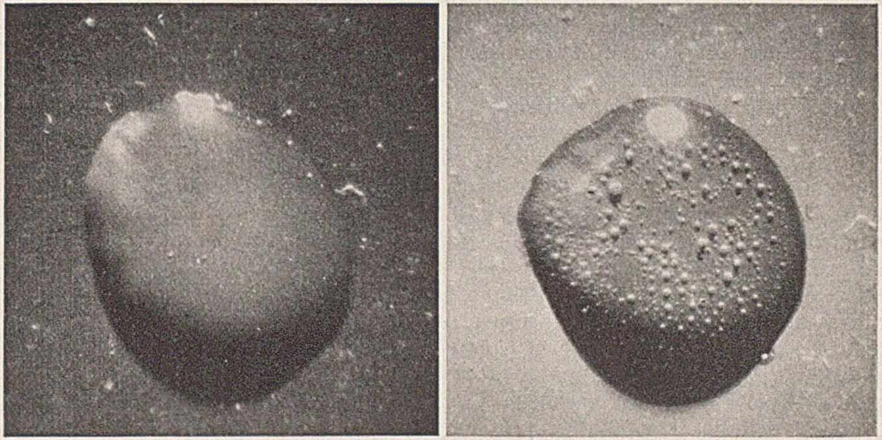
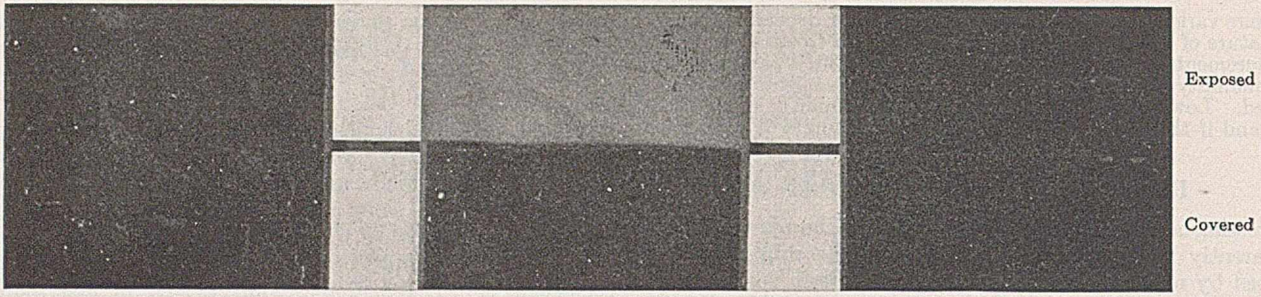


Figure 3. A Drop of Dilute Hydrochloric Acid on (*left*) an Unfrosted and (*right*) a Frosted Rubber Surface Containing Whiting

Figure 2 (left) shows a photomicrograph of the surface of a glossy black rubber compound. The clear blackness results from the absorption of light by the black pigment under the continuous, transparent rubber surface. The same surface is



0.35 part of 4,4′-diamino-diphenylmethane per 100 parts of rubber.

Air-cured rubber control, no protective agent.

0.50 part of antifrosting wax per 100 parts of rubber.

FIGURE 4. EFFECT OF ANTIFROSTING CHEMICALS

shown at the right after it has been frosted. The granular appearance is due to the reflected light from the disintegrated and cracked surface. The larger objects on the surface are dust or pigment particles picked up during handling.

In severe frosting the ozone disintegration of the surface exposes some filler particles which further interfere with the transmission of light and increase light diffusion. If a frosted rubber stock contains whiting, it can easily be demonstrated that the pigment particles are exposed by treating with dilute acid and observing the evolution of carbon dioxide. Zinc and other elements extractable by aqueous acids can be detected in an acid extract of the frosted surface. In an unfrosted or bloomed surface, the pigment particles are coated by a film of rubber and are not so easily attacked by dilute acids. Extraction of a pigment from a frosted surface does not restore the original appearance.

Figure 3 (left) shows a drop of dilute hydrochloric acid on an unfrosted surface. At the right a similar drop of acid is shown on the same rubber sample after frosting. This rubber compound contained whiting and the gas bubbles visible in the drop of acid are carbon dioxide being evolved from the frosted surface. The acid is prevented from reacting with the pigment in the unfrosted sample by the continuous rubber surface.

Prevention of Frosting

Rubber vulcanized with aldehyde-amine accelerators seems to be more resistant to frosting than rubber vulcanized with the thiazoles, dithiocarbamates, and guanidines which are now more widely used. It is believed that frosting was not encountered until recent years because the accelerators formerly used produced vulcanized rubber less sensitive to ozone than is obtained with the present accelerators.

Frosting can obviously be prevented by any protective film which excludes ozone from contact with the rubber. Varnished and lacquered surfaces do not frost. Also chemical treatments which reduce the chemical reactivity of the surface will reduce its tendency to frost. Treatments with chlorine, bromine, or sulfur monochloride are effective.

Frosting is also inhibited by incorporating a small proportion of certain high-melting special petroleum waxes which bloom to the surface and form a protective film. Casper wax (*2*) from a Wyoming petroleum field is most effective. Ordinary paraffin is without effect. Excessive wax bloom may affect the adhesive qualities of the unvulcanized rubber or the finish after vulcanization. One half per cent of wax on the rubber can generally be used without a noticeable bloom but this is not sufficient to give complete protection against frosting and atmospheric cracking.

A large number of chemicals have been investigated for inhibiting frosting by the laboratory frosting test. It is noteworthy that the chemicals which have been found to inhibit frosting in the laboratory accelerated test have confirmed this result under natural frosting conditions. Some aldehyde-amine and ketone-amine antioxidants are sometimes slightly effective in inhibiting frosting. Most of the usual types of antioxidants and antiflex-cracking agents are entirely without effect. A limited number of chemicals have been found which are of any value. The most effective of these are all members of one class, the diprimary aryl amines, represented by *p*-phenylene diamine, benzidine (4,4′-diaminodiphenyl), and 4,4′-diaminodiphenylmethane.

p-Phenylene diamine and benzidine are toxic chemicals unsatisfactory for commercial use. 4,4′-Diaminodiphenylmethane has some antioxidant properties and gives some activation of the cure for which allowance should be made. It has been in commercial use for a number of years and is far superior to other known antifrosting chemicals.

The effect of these antifrosting agents is shown in Figure 4. These samples were subjected at the same time to ozonized air in the frosting chamber with the lower half of each sample covered with tin foil. The protective action of the added chemicals is clearly demonstrated.

This discussion of frosting should not be completed without emphasizing that it is only one of the causes for objectionable changes in the finish of vulcanized rubber products but it should be suspected in any case not obviously of another type.

Literature Cited

(1) Allen, IND. ENG. CHEM., Anal. Ed., 2, 55 (1930).
(2) Bradley and Mason, U. S. Patent 1,832,964 (Nov. 24, 1931).
(3) Memmler, "Science of Rubber", Am. Ed., p. 210 (1934).
(4) Reynolds, *J. Soc. Chem. Ind.*, 49, 168–72T (1930).
(5) Sheehan and Carmody, IND. ENG. CHEM., Anal. Ed., 9, 8 (1937).
(6) Taylor, "Treatise on Physical Chemistry", p. 1286, New York, D. Van Nostrand Co., 1925.
(7) Van Rossem and Talen, *Rubber Chem. Tech.*, 4, 490 (1931).
(8) Williams, IND. ENG. CHEM., 18, 367 (1926).

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Rotameter Flow Rates—Correction

In our paper "Correlation of Rotameter Flow Rates" which appeared on pages 451–6 of the April, 1939, issue, we find that some confusion has arisen as to units employed. In the master plot of calibration data (Figure 3) the capacity of the meter, q, was expressed as cubic inches/minute. On taking slopes from this plot for correlation purposes, the dimensions of the slopes were converted from square inches/minute/minute to square inches/second/second by dividing by 3600; the handling of extremely large numbers was thus avoided. The value of $2gL$ (423) was determined from $g = 386.4$ inches/second/second, and L as inches; therefore 423 was added to the above determined slope to give the constant C. C' ($= C\rho$) was determined from this C; ρ and all other dimensions were as stated in the nomenclature.

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Entrainment in Plate Columns

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MODERN design of plate columns frequently calls for the use of vapor velocities sufficiently high so that the effect of entrainment on column performance cannot be neglected. The method of calculating the required number of plates in columns when entrainment is an important factor has been treated by Sherwood and Jenny (*4*), Colburn (*1*), Rhodes (*3*), and others.

The purpose of this paper is to present a modification of the method of Sherwood and Jenny for binary systems. This modification seems to possess some merit from the viewpoint of simplicity, particularly as applied to the teaching of distillation calculations.

When there is no entrainment, a general material balance on the assumption of constant molal overflow results in the following equations for the upper and lower operating lines on the McCabe-Thiele diagram (*2*):

$$V_n y_n = L_n x_{n+1} + D x_d \qquad (1)$$

or

$$y_n = \frac{L_n}{V_n} x_{n+1} + \frac{D x_d}{V_n} \qquad (1a)$$

$$V_m Y_m = L_m x_{m+1} - W x_u \qquad (2)$$

or

$$y_m = \frac{L_m}{V_m} x_{m+1} - \frac{W x_w}{V_m} \qquad (2a)$$

If one mole of vapor entrains or carries up the column *e* moles of liquid, a general material balance yields the following equations for the operating lines:

$$V_n y_n + e V_n x_n = (L_n + e V_n) x_{n+1} + D x_d \qquad (3)$$

or

$$y_n = \frac{L_n}{V_n} x_{n+1} + \frac{D x_d}{V_n} + e(x_{n+1} - x_n) \qquad (3a)$$

$$V_m y_m + e V_m x_m = L_m x_{m+1} + e V_m x_{m+1} - W x_w \qquad (4)$$

or

$$y_m = \frac{L_m}{V_m} x_{m+1} - \frac{W x_w}{V_m} + e(x_{m+1} - x_m) \qquad (4a)$$

V and *L* in Equations 3 to 4a, inclusive, refer to the quantity of dry vapor and to the quantity of reflux resulting from it. If there is zero entrainment, the last terms of Equations 3a and 4a drop out, and these equations become identical with Equations 1a and 2a.

For a system and conditions that make 1a and 2a equations of straight lines, Equations 3a and 4a are equations of curved lines, since neither $(x_{n+1} - x_n)$ nor $(x_{m+1} - x_m)$ are linear with x due to the curvature of the equilibrium curve. Further, for any given value of x_{m+1}, a point on the line of Equation 3a will lie above a point on the line of Equation 1a by the amount $e(x_{n+1} - x_n)$. Likewise, for any given value of x_{m+1}, a point on the line of equation 4a will lie above a point on the line of Equation 2a by the amount $e(x_{m+1} - x_m)$. Figure 1 shows a simple method of constructing these curved operating lines to meet the above requirements. Figure 1 is constructed for the conditions:

Composition of feed:	$x_f = 0.50$
Composition of distillate:	$x_d = 0.95$
Composition of waste:	$x_w = 0.05$
Thermal condition of feed:	$q = 0.50$
Reflux ratio:	$V_n/D = 2.70$
Relative volatility	$= 4.0$
Entrainment:	$e = 0.40$

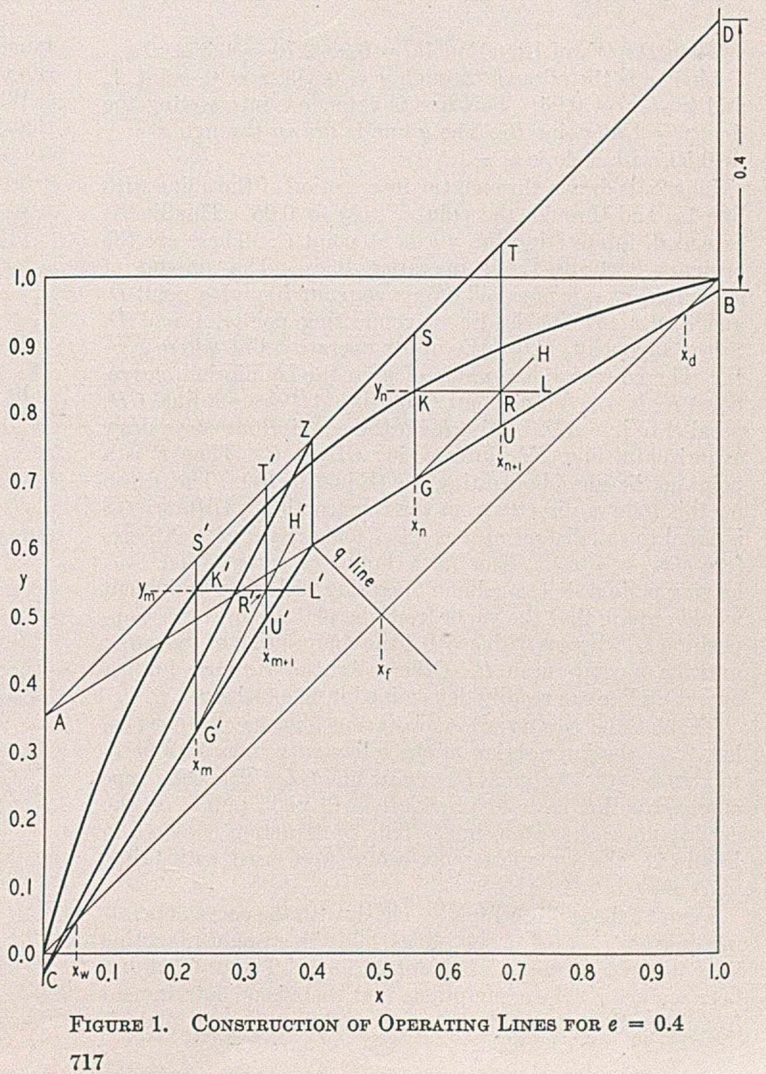

FIGURE 1. CONSTRUCTION OF OPERATING LINES FOR $e = 0.4$

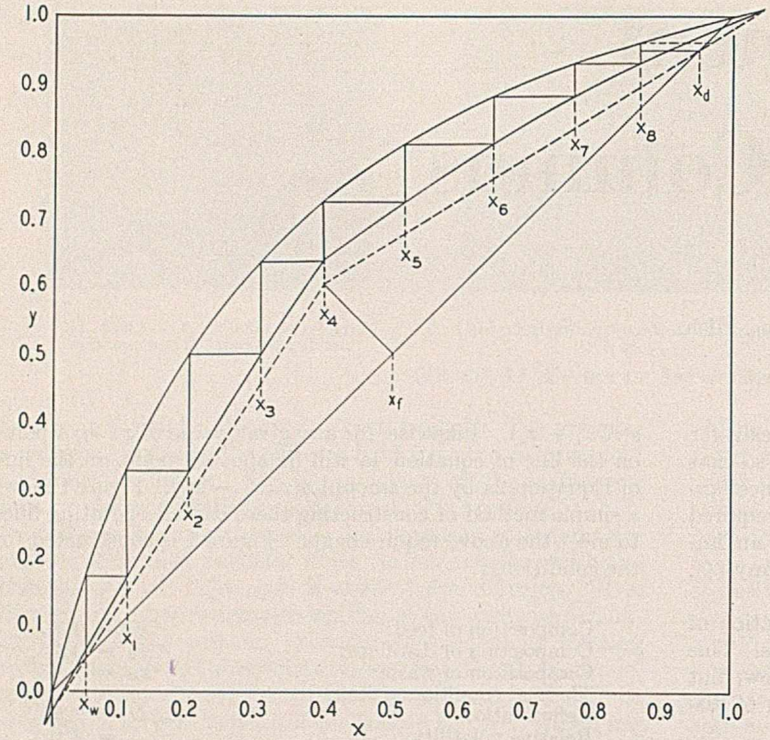

FIGURE 2. DETERMINING THE NUMBER OF THEORETICAL PLATES FOR $e = 0.4$

Then Dx_d/V_n of Equation 1a $= 0.95/2.70 = 0.352$.

Line 1a is then drawn through $y = 0.352$, $x = 0$, point *A*, and $x = y = 0.95$. This line is extended, intersecting the line $x = 1$ at point *B*. The *q* line is drawn through $x = y = 0.50$, with a slope of -1.

Line 2a is drawn through the intersection of the *q* line with line 1a, and through the point $x = y = 0.05$. This line is extended, intersecting the *y* axis at point *C*. These are the ordinary McCabe-Thiele operating lines. The amount of entrainment, *e*, is now laid off above point *B*, giving point *D*, and a straight line is drawn connecting points *A* and *D*. Select any point, *G*, on the upper operating line where $x = x_n$. The corresponding value of *y* on the equilibrium curve, point *K*, is y_n. From point *G* on line *AB* draw a line, *GH*, parallel to line *AD*. From *K* on the equilibrium curve draw a horizontal line, *KL*, intersecting *GH* at *R*. Then *R* is a point on the curved operating line (Equation 3a). The reason for this follows directly from the construction. Distance *GS* is equal to ex_n, distance *UT* is ex_{n+1}, and distance *UR* is therefore $e(x_{n+1} - x_n)$. Thus for a liquid of composition x_{n+1} leaving plate $n + 1$, a column operating without entrainment would require that the vapor from the plate below be of composition *U*, whereas with $e = 0.4$ the composition of the vapor must be of composition *R*. Other points on the curved upper operating line are readily determined in like fashion.

To plot the curved lower operating line, erect a vertical line from the intersection of the *q* line with lines 1a and 2a to give point *Z* on line *AD*. Draw line *CZ*. The same type of construction as used previously will yield points on the curved lower operating line. This construction is shown in Figure 1; the same letters as before were used with prime mark added.

Figure 2 shows the completed chart, with the curved operating lines for $e = 0.4$ in solid lines, and the straight operating lines for zero entrainment as dotted lines. The problem has been worked on the assumptions that there is no entrainment from the still, and that the spacing above the top plate is sufficient so that there is no entrainment in the vapor going to the single total condenser. From this condenser, product is withdrawn and reflux at the boiling point is returned to the column. It should be noted that these conditions call for using lines 1a and 2a for the stepwise construction at $x = x_w$, and at $x = x_d$ as shown in Figure 2. With zero entrainment, 6.4 theoretical plates are required, and 8.6 theoretical plates with 0.4 entrainment.

If the entrainment in the upper and lower parts of the column is not the same, the construction would obviously be slightly modified to meet this situation. Thus, if the entrainment in the lower part of the column were 0.5, the entrainment in the upper part remaining 0.4, the spread between line 2a and line *CZ* would be increased in the ratio of 5 to 4 over that shown in Figure 1.

The curved operating lines intersect the normal operating lines at the points where extensions of the equilibrium line below $x = 0$ and above $x = 1.0$ intersect the normal operating lines for zero entrainment. The two curved operating lines themselves intersect on the vertical through the intersection of the *q* line with the normal operating lines.

If it is desired to apply Murphree plate efficiencies to the stepwise calculation to determine directly the numbers of actual plates required, this is readily done by proportioning the distance between the curved operating lines and the equilibrium curve.

While the method presented is not basically new, it is hoped that it will prove of advantage.

Nomenclature

D = moles of distillate in unit time
F = moles of feed in unit time
L_n = moles of reflux above feed plate in unit time, not including the returned entrainment
L_m = moles of reflux ($L_n + qF$) below feed plate
V_n = moles dry vapor above feed plate in unit time $= V_m + (1 - q)F$
V_m = moles dry vapor below feed plate
W = moles of waste (bottoms) in unit time
e = moles of liquid entrained by vapor per mole of vapor
q = moles of liquid resulting on feed plate, per mole of feed, from introduction of feed
x = mole fraction of more volatile substance in liquid
y = mole fraction of more volatile substance in vapor

Subscripts

d = distillate
w = waste
m = any plate in lower part of column
$m + 1$ = plate above *m*th plate
n = any plate in upper part of column
$n + 1$ = plate above *n*th plate.

Literature Cited

(1) Colburn, A. P., IND. ENG. CHEM., 28, 526–30 (1936).
(2) McCabe, W. L., and Thiele, E. W., *Ibid.*, 17, 747 (1925).
(3) Rhodes, F. H., *Ibid.*, 26, 1333 (1934), 27, 272 (1935); Rhodes, F. H., and Slachman, P. G., *Ibid.*, 29, 51 (1937).
(4) Sherwood, T. K., and Jenny, F. J., *Ibid.*, 27, 265–72 (1935).

Film Continuity of Synthetic Resin Coatings

Effect of Composition and Chain Length on Minimum Coating Weights for Methacrylate Polymers

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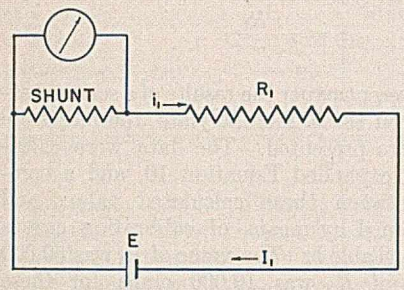
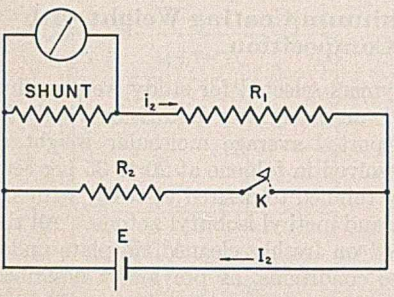
Minimum coating weight studies on three experimental methacrylate polymers of varying composition and varying average chain lengths show that the coating weight required to just produce continuity seems to vary inversely with the chain length and directly with the effective polarity. This relation was previously shown to be valid for vinyl acetate and vinyl chloride copolymers.



EFFECTIVE CIRCUIT WITH K OPEN



EFFECTIVE CIRCUIT WITH K CLOSED

Figure 1. Effective Circuits

IN THE first paper in this series (2) a method for the rapid determination of the "continuity" of resin films was described. In this and later contributions (3, 4) it was shown that the minimum thickness of film required to produce such continuity might be related to the activity of the metal being coated, to the average molecular weight of the resin, and to its composition.

The experimental technique and apparatus were discussed previously (2). It was pointed out that the use of the equation given by Carhart and Patterson (1) for the measurement of high internal resistances introduces inaccuracies in "observed" resistances which increase with the magnitude of the resistances being measured; it was shown (2, 3) that this is to be expected when Carhart and Patterson's limiting assumptions are considered. At that time the apparatus was calibrated against known resistances over its usual working range, and corrected internal resistance values were obtained by use of the calibration curves.

The approximated equation which Carhart and Patterson suggest for internal resistance measurements is derived by them as follows (1):

> Let d_1 be the deflection of the galvanometer when the circuit is closed through the high resistance (R_1), the key K being left open; and let d_2 be the deflection when key K is closed (see Figure 1). The two deflections are proportional to the currents through the galvanometer, and therefore to the P. D.'s at the terminals of the shunt, with K open and closed, respectively. Since the shunt bears a constant ratio to the entire resistance in circuit, the deflections d_1 and d_2 are proportional to the P. D.'s at the battery (cell) terminals in the two cases. Hence,
>
> $$d_1 : d_2 = E : E' = (R_2 + r) : R_2 \qquad (1)$$
>
> When the key K is open, the P. D. at the battery terminals, measured by d_1, is the entire e. m. f. of the cell if its internal resistance is negligible in comparison with the high resistance in circuit; and when K is closed, the P. D. measured by d_2 is the fall of potential over the external resistance R. Now if the e. m. f. of the cell does not change immediately on closing K, then the fall of potential over the entire resistance, $R + r$, is the e. m. f. of the cell. We may, therefore, put the two deflections proportional to the resistances (Equation 1). From Equation 1 by subtraction,
>
> $$(d_1 - d_2) : d_2 = r : R_2 \qquad (2)$$
>
> whence
>
> $$r = R_2 \frac{d_1 - d_2}{d_2} \qquad (3)$$

An earlier paper (3) showed that Equation 3 gives accurate values only in low resistance ranges, and that only as the magnitude of R_1 approaches infinity can the equation be considered quantitative.

Corrected Equation for Calculating Internal Resistances

Although the use of calibration curves for the several combinations of R_1 and R_2 employed in this laboratory to determine actual resistances from values obtained from Equation 3 is satisfactory, the desirability of expanding the equation to

TABLE I. COATING CONTINUITY *vs.* FILM WEIGHT

Sample No.	Coating Wt. *Mg./sq. in.*	Potential *Volt*	d_1	d_2	Internal Resistance: Cor. by curve *Ohms*	Internal Resistance: Calcd. from Equation 10 *Ohms*	$E/R_{\text{calcd.}}$ *Microamp.*
Methyl Methacrylate							
1	5.07	Deflection too low to read			>500,000	.....	<1.0
2	4.38	0.663	1.4	0.3	145,000	137,500	4.8
3	3.20	0.584	2.8	1.3	17,500	15,000	38.9
4	2.45	0.591	2.9	1.6	9,000	9,720	61.0
5	2.21	0.582	3.1	1.6	11,000	11,530	50.4
6	1.70	0.655	2.2	0.7	40,000	37,500	17.5
7	1.48	0.653	3.1	1.7	10,000	9,875	66.2
8	1.18	0.729	3.2	1.7	10,500	10,725	68.0
9	0.80	0.843	3.5	2.1	7,500	7,680	110.0
10	0.62	0.761	3.6	2.2	7,000	7,290	104.5
11	0.00	0.764	9.6	7.5	2,900	2,975	257.0
n-Propyl Methacrylate							
1	9.24	...	Film continuous			.....	...
2	6.74	...	Film continuous			.....	...
3	6.02	...	Film continuous			.....	...
4	4.61	Deflection too low to read			>500,000	.....	<1.0
5	3.62	Deflection too low to read			>500,000	.....	<1.0
6	2.81	0.783	1.9	0.6	40,000	38,200	20.5
7	1.68	0.659	2.5	1.1	17,000	17,100	38.8
8	0.00	0.764	9.6	7.5	2,900	2,975	257.0
n-Butyl Methacrylate							
1	13.77	...	Film continuous			.....	...
2	12.00	...	Film continuous			.....	...
3	10.95	...	Film continuous			.....	...
4	8.75	...	Film continuous			.....	...
5	6.84	...	Film continuous			.....	...
6	4.33	0.782	3.6	0.8	115,000	116,500	6.7
7	3.20	0.627	10.6	4.6	17,500	17,650	35.5
8	1.45	0.572	11.7	5.9	11,500	12,250	46.7
9	0.00	0.764	9.6	7.5	2,900	2,975	257.0

yield accurate values over a wide range of measured resistances is obvious. Accordingly, a general equation was derived which is independent of the limiting assumptions employed by Carhart and Patterson.

In Figure 1, let i_1 be the current which flows through the galvanometer with K open, and I_1 the current through the cell leads into the high resistance. Then,

$$i_1 = I_1 = kd_1 \qquad (4)$$

Let i_2 be the current which flows through the galvanometer when K is closed, and I_2 the current through the cell leads into the parallel resistance circuit. Then,

$$i_2 = \frac{R_2}{R_1 + R_2} I_2 = kd_2 \qquad (5)$$

Let $r_{\text{int.}}$ be the cell internal resistance; R_t, the circuit resistance with K closed, equal to $R_1R_2/(R_1 + R_2)$; and E be the cell e. m. f.:

$$(K \text{ open})\ E = I_1r_{\text{int.}} + I_1R_1 \qquad (6)$$

$$(K \text{ closed})\ E = I_2r_{\text{int.}} + I_2R_t \qquad (7)$$

Equations 6 and 7 may be equated if we assume no marked change in E due to polarization during the brief time required to read deflection d_2. The inherent error introduced by making this assumption is well within the limits of experimental error. Accordingly,

$$I_1r_{\text{int.}} + I_1R_1 = I_2r_{\text{int.}} + I_2\frac{R_1R_2}{R_1 + R_2} \qquad (8)$$

Substituting Equations 4 and 5 in 8, and clearing of common terms,

$$r_{\text{int.}}\left(\frac{R_1 + R_2}{R_2} d_2 - d_1\right) = R_1(d_1 - d_2) \qquad (9)$$

$$r_{\text{int.}} = \frac{R_1(d_1 - d_2)}{\frac{R_1 + R_2}{R_2} d_2 - d_1} \qquad (10)$$

Finally, we may make use of the simplified relationship in Equation 3 to derive an equation relating the "observed" internal resistance to the true resistance, as follows: Let r' be the resistance calculated from Equation 3, and r be the resistance calculated from Equation 10. Then,

$$\frac{r'}{R_2} = \frac{d_1 - d_2}{d_2} = Q \qquad (11)$$

It can be shown that

$$Q = \frac{r(R_1)}{R_2(r + R_1)} \qquad (12)$$

Whence, equating (11) and (12),

$$r = \frac{r'R_1}{R_1 - r'} \qquad (13)$$

In the present paper the results of a series of experiments on three methacrylate thermoplastic polymers are presented. The data were calculated from expanded Equation 10, and a comparison between these calculated values and those obtained by means of calibration curves are given in Table I. The value of R_1 was 50,000 ohms and of R_2 was 10,000 ohms for these experiments.

Variation in Minimum Coating Weight with Composition

The three linear polymers selected for study were methyl methacrylate, *n*-propyl methacrylate, and *n*-butyl methacrylate. All had a reported average molecular weight of 40,000. They were dissolved in toluene at 20 to 35 per cent solids and subsequently thinned to desired viscosity with a 1 to 1 mixture of toluene and methyl isobutyl ketone. All the samples were dip-coated on freshly cleaned tin plate under dust- and moisture-free conditions, as previously described (*2*). The weight taken up was controlled by varying the withdrawal speed and by successive thinning with 1 to 1 toluene–methyl isobutyl ketone. Coating weights were determined as before by weighing measured areas cut from duplicate panels, stripping with acetone, and reweighing. The coated panels were baked for 15 minutes at 300° F. Data on cell resistance as a function of coating weight are summarized in Table I.

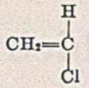
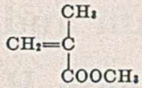
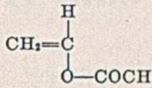
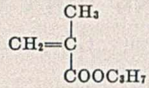
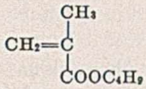
Curves showing the relation between film continuity and coating weight are plotted in Figure 2. The extrapolated points for coating weights to just produce complete continuity on tin plate are as follows (in mg. per square inch):

Methyl methacrylate	4.8–5.8
n-Propyl methacrylate	4.0–5.0
n-Butyl methacrylate	4.5–5.5

Molecular Weight *vs.* Chain Length in Determining Minimum Coating Weights

The above estimated minimum coating weights may seem inordinately high for linear polymers of 40,000 average molecular weight. Actually, they are of the proper order of magnitude, when average chain length is taken into consideration rather than over-all molecular weight. An earlier paper (*3*) showed that the weight of film to just produce continuity is an inverse function of average molecular weight, when polymers of the same basic structural unit are compared. Valid

Table II. Composition of Typical Linear Polymers

Monomer	Structure	Mol. Wt. Total	Mol. Wt. Side chain	Distribution In side chain %	Distribution In linear chain %	Polymer Av. mol. wt.	Polymer Av. linear chain length C atoms	Min. Coating Wt. Mg./sq. in.
Vinyl chloride	 $CH_2{=}\overset{H}{\underset{Cl}{C}}$	62	36	58.0	42.0	28,000	900	2.8–3.8
Methyl methacrylate	 $CH_2{=}\overset{CH_3}{\underset{COOCH_3}{C}}$	100	74	74.0	26.0	40,000	800	4.8–5.8
Vinyl acetate	 $CH_2{=}\overset{H}{\underset{O-COCH_3}{C}}$	86	59	68.5	31.5	27,000	630	5.5–6.5
n-Propyl methacrylate	 $CH_2{=}\overset{CH_3}{\underset{COOC_3H_7}{C}}$	128	102	80.0	20.0	40,000	626	4.0–5.0
n-Butyl methacrylate	 $CH_2{=}\overset{CH_3}{\underset{COOC_4H_9}{C}}$	142	116	81.5	18.5	40,000	620	4.5–5.5

comparisons between different polymers can be made only on the basis of effective chain length.

Table II lists a number of monomeric units which polymerize to thermoplastic chain-type polymers, together with the experimentally determined minimum coating weights obtained in this laboratory.

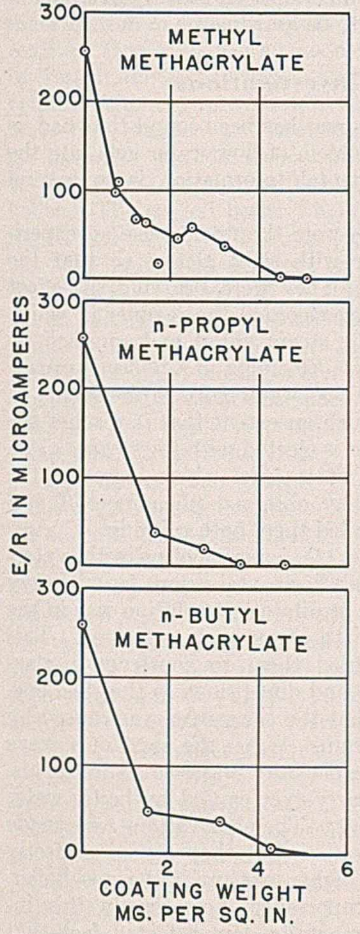


Figure 2. Relation between Film Continuity and Coating Weight

Effect of Polarity on Minimum Coating Weight

In order to compare polymers of different effective polarity, it is necessary to select those of approximately equal chain lengths. Thus, referring to Table II, we may compare the *n*-propyl methacrylate with the *n*-butyl methacrylate polymer and with polyvinyl acetate. Consideration of the atomic arrangement of the actively polar carbonyl group in the methacrylate polymers with respect to the linear chain, as compared with the arrangement in polyvinyl acetate, would perhaps indicate that the latter should be slightly more polar than the methacrylate polymers. Accordingly, one might expect to find a slightly higher minimum coating weight for polyvinyl acetate than for the methacrylates, and this is found by experiment.

A slight difference was found between *n*-propyl methacrylate and *n*-butyl methacrylate. The shift in minimum coating weight is in the direction that might be predicted on the basis of alternation for the atoms in the respective side chains (such as is manifested in dipole moment measurements, for example). The experimental data do not warrant valid conclusions to be drawn on this point; the difference lies within the margin of experimental error.

Finally, it is of interest to compare the minimum coating weight for the relatively nonpolar polyvinyl chloride with that for methyl methacrylate. Although the experimental resins differ in effective average chain length by only 11 per cent, the minimum coating weights are separated widely, and lie well outside experimental error. This seems to be added evidence that continuity may be directly related to effective polarity.

Acknowledgment

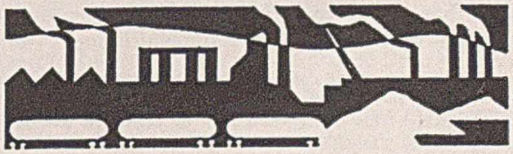
The authors wish to express their appreciation to A. K. Doolittle and R. W. Quarles, Carbide and Carbon Chemicals Corporation, who are responsible for the derivation of the general equation for the internal resistance of the cells.

This paper is a contribution from the Stoner-Mudge, Inc., Industrial Fellowship at Mellon Institute.

Literature Cited

(1) Carhart, H. S., and Patterson, G. W., "Electrical Measurements", pp. 98–100, Boston, Allyn and Bacon, 1895.
(2) Young, G. H., and Gerhardt, G. W., Ind. Eng. Chem., 29, 1277 (1937).
(3) Young, G. H., Gerhardt, G. W., Schneider, W. K., and Seagren, G. W., *Ibid.*, 30, 685 (1938).
(4) Young, G. H., Schneider, W. K., and Gerhardt, G. W., *Ibid.*, 29, 1280 (1937).

Contribution from the Stoner-Mudge, Inc., Industrial Fellowship at Mellon Institute.



FOAMING OF BOILER WATER

Manner in Which Water Enters Steam and Conditions Affecting Foam Height[1]

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This paper describes experiments with two widely different experimental boilers equipped with sight glasses to give a view of the interior. In both boilers, and with all of the synthetic boiler waters tried, the mechanism of gross carry-over was always the drawing into the steam of foam on the surface of the water. This was at times brought about by the surging up of the water which lifted the foam layer on top.

When the concentrations of dissolved salts were pushed to high values, in most cases the thickness of the foam layer passed through a maximum.

The inconsistencies in the use of the words "foaming" and "priming" are also pointed out.

FOR many years the carry-over of liquid water into the steam line of an operating boiler has been ascribed to one or more of the following phenomena:

I. The formation of a sufficiently thick layer of foam on the surface of the boiler water to reach the steam outlet.
II. Violent ebullition or other mechanical agitation that throws slugs of water against the steam outlet.
III. Lifting of the boiler water by the sudden formation of steam bubbles throughout its mass.

These descriptions of the behavior of boiler water are not based on direct observation, because no commercial boiler has ever been equipped with sight glasses that give a view of the space between the water and the steam outlet. The water level gage glass does give some evidence of the behavior of the water, but it does not afford a view of the interior of the boiler. These three ways, then, in which water is said to reach the steam line must be looked on as speculations rather than as observed phenomena. They are, however, sagacious speculations because, as shown below, experiments with high-pressure laboratory boilers equipped with sight glasses have confirmed them to a large extent. These laboratory experiments have also suggested a new question—namely, which of the three phenomena occurs most frequently. The importance of this question can be stated as follows: Two of the three ways (the formation of a layer of foam and the filling of the mass of water with steam bubbles) are chemical phenomena and therefore call for chemical investigation. The upward projection of slugs of water, however, is a mechanical phenomenon, which makes it a mechanical problem.

"Foaming" and "Priming"

The authors wish to point out that they deliberately omitted the words "foaming" and "priming" from their descriptions of boiler phenomena. The reason is that consistent definitions of these words have not yet crystallized in the literature of boiler water chemistry. What one writer calls foaming another calls priming. Some writers call foaming a special case of priming and some call priming a special case under foaming. This chaotic condition was pointed out in 1924 by Foulk (*4*), and since then most writers define the terms as they use them. To say categorically that this phenomenon is priming and that one is foaming is merely adding to the confusion. Fortunately, the use of the word "carry-over" to cover all situations that result in liquid water in the steam appears to be growing.

Previous Investigations

No investigation of carry-over has been found that had as its original objective the problem of how water gets into the steam. Nevertheless, incidental information is in several papers.

Joseph and Hancock (*13*) were the first to use an experimental high-pressure boiler with sight glasses so that the interior could be observed. They were studying the effect of suspended solids, but they recorded the manner in which the boiler water reached the steam outlet and summed up their observations as follows: "Priming in a boiler is caused by the layer of bubbles on the water surface increasing in thickness and stability to such an extent that it reaches the steam exit pipe so that water is ejected with the steam. It is accompanied by a rise in water level which increases the effect." In other words they observed phenomena I and III, but not II; and they called them both priming.

In 1933 Foulk and Groves (*7*), experimenting with a steel water tube boiler with a long horizontal drum, found heavy carry-over if distilled water or dilute salt solution was in the boiler and no carry-over with strong salt solutions. This anomalous behavior prompted them to construct a glass boiler with the same design and dimensions as the steel one. Observation then showed that the carry-over was caused by waves moving along the drum. When the crest of a wave hit the steam outlet, a slug of water was carried in. This, then, was a clear case of carry-over caused by boiler water thrown against the steam exit. The observations were made in glass at atmospheric pressure, but they agreed perfectly with the results obtained at higher pressure in the steel boiler.

The point of greatest importance, however, in this investigation was the experimentally demonstrated fact that the high waves were associated with distilled water and dilute solutions and were caused by pulsations set up by large

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[1] Nearly all experimental details have been omitted from this paper. They are recorded in John W. Ryznar's doctor's dissertation. The conditions under which this dissertation may be consulted can be obtained from the Library of The Ohio State University.

steam bubbles entering the drum from the water tube. In the strong salt solutions, however, the steam bubbles were small and the waves were low. (The theory of the production of small bubbles in salt solutions is given in a paper by Foulk and Miller, *8*.) It was thus shown that foaming conditions in the boiler were the determining factors in what appeared, at first sight, to be purely mechanical effects due to the design of the boiler.

In addition, the senior author has received one or two personal accounts of old-fashioned horizontal boilers that gave less carry-over with concentrated than with fresh boiler water.

More detailed studies of carry-over made during the last few years have suggested a fourth way in which water may get into the steam. This is the upward projection of droplets which accompanies the bursting of bubbles on the surface of a liquid. It is a reasonable supposition that this occurs in a boiler and is the cause of the small amount of moisture usually in the steam. The first reference to this in boiler water chemistry is by Foulk (*5*) who also gives its cause (*6*).

Whether or not such projected droplets are carried into the steam is a function of the steam velocity. Cassidy (*1*) in discussing this question gives an equation for what he calls the "critical steam velocity" which he defines as "the velocity which will suspend the particle in the steam, and above which the particle will be lifted by the steam."

Finally, the mists or fogs described later in this paper may possibly be a fifth cause of moisture in steam.

Boilers

Two widely different experimental boilers were used in this investigation in order to reduce the influence of design on the results. One of them was modeled after the boiler employed by Joseph and Hancock (*13*) and may be described as a steel cylinder with a glass window in each end. It was used in the horizontal position and heated from below with air-driven gas burners. Full details are given by Foulk and Whirl (*10*). In the present paper it will be referred to as the cylindrical boiler. The second boiler was, in general, like the one designed and built by Christman, Holmes, and Thompson (*2*), but was larger and different in a few details, as Figure 1 shows. It is referred to in this paper as the water tube boiler. In both boilers the steam outlet was a pipe [inside diameter, 1.9 cm. (0.75 inch) in the cylindrical boiler and 2.5 cm. (1 inch) in the water tube boiler] that extended downward into the steam space to a point below the sight glasses. This made it possible to observe how the boiler water reached the steam line.

PROCEDURE. The general procedure was to pump salt solution into the boiler while it was steaming. In this way the concentration of the boiler water was gradually increased until an Ulmer apparatus (*15*) indicated gross carry-over—that is, the presence of several per cent of boiler water in the condensed steam. The rate of evaporation was 475 cc. per minute, and the pressure, unless otherwise stated, was 17.6 kg. per sq. cm. (250 pounds per square inch) in the water tube boiler and 10.5 kg. per sq. cm. (150 pounds per square inch) in the cylindrical boiler. The distance of the steam outlet from the water was 9 cm. (3.5 inches) in both boilers.

The synthetic boiler waters used were solutions of sodium chloride, sodium sulfate, sodium carbonate, sodium aluminate, calcium chloride, and magnesium chloride. In a few cases solid matter was also added.

Since the object of the research was to determine by which of the usually accepted ways (I, II, or III) the water reached the steam exit, all that was done was to increase the concentration of the salt in the boiler water until gross carry-over occurred and at the same time observe through the sight glasses the manner in which the boiler water entered the steam outlet. In other words, purely qualitative observations were made.

How Water Reaches Steam Line

In all the experiments, with both boilers and with all of the synthetic boiler waters employed, the mechanism of gross carry-over was always the entrance of foam into the steam outlet, and it always occurred suddenly. During an experiment the Ulmer apparatus frequently showed a few hundredths or tenths of a per cent of water in the steam, but there was no gradual increase from this to the several per cent called "gross" carry-over.

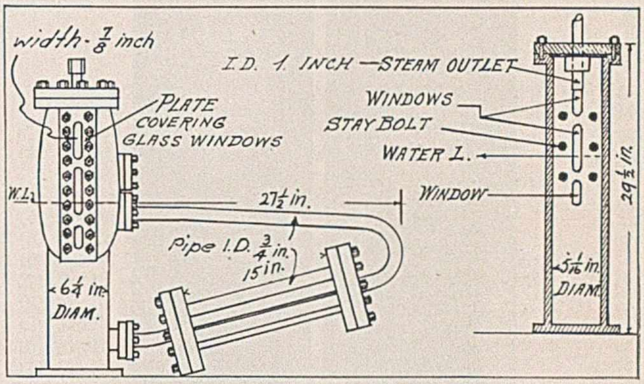

FIGURE 1. WATER TUBE BOILER

Three modes of approach of the foam to the steam pipe, however, were observed:

1. The layer of foam grew deeper as the concentration of dissolved salt in the water increased, until it covered the steam outlet. This deepening of the foam layer followed the well-known conditions that cause an increase in foaming and therefore needs no further discussion.
2. The layer of foam without becoming thicker was lifted against the steam outlet by an upward surge of the water. This surging up and down or rapid lifting of the boiler water varied somewhat with the nature of the salt in solution and with the concentration. Calcium chloride solutions, for example, surged more than the solutions of the other salts. Another instance of the erratic behavior of calcium salts is given by Foulk and Ulmer (*9*).

   This surging, which occurred in both boilers, seemed to go through a maximum; that is, it increased with the concentration in the dilute salt solutions and decreased in the concentrated ones. Time, however, did not permit a separate study of this behavior, and therefore no hypothesis is offered to explain it.
3. Foam was sucked into the outlet pipe from a distance of 1 or 2 cm. from the foam layer if the outflow of steam was very rapid. This behavior was observed in the cylindrical boiler only. It could be induced by suddenly opening the steam valve.

No gross carry-over occurred unless the steam outlet was completely covered with foam. Mode 3, however, gives an exceptional case.

Appearance of Foam

Many observations on the appearance of the foams were made, but there is little point in recording them here because no relation seemed to exist between the looks of the foam and the carry-over. In general, the bubbles were smaller and more nearly uniform in size at the higher than at the lower concentrations. The most interesting observation was that the bubbles in the dilute solutions of calcium and magnesium chlorides were football-shaped, whereas at the higher concentrations they were spherical as in the other salt solutions. Steam bubbles so elongated that some of them are cigar-shaped are shown in photographs made for the Dampney Company of America by K. J. Germenhausen, with an exposure of 0.00001 second. They are reproduced in an article on heat transfer and condensation by Jakob (*12*).

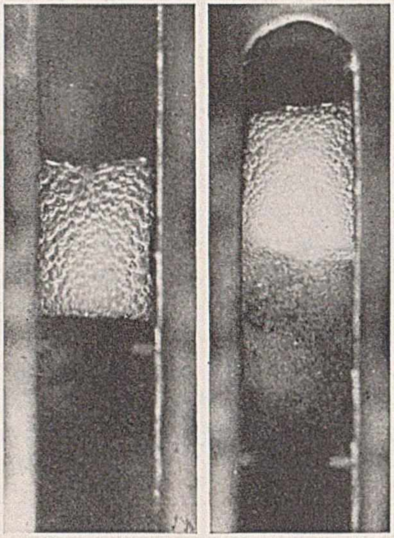

Figure 2. Foam on Solution of Sodium Chloride in Water Tube Boiler

Left, 5000 and *right,* 30,000 p. p. m. of sodium chloride

Figure 2 shows the differences in foams at low and high concentrations. These are probably the first published photographs of solutions boiling at 250 pounds pressure and over 200° C.

Less Foam at High Concentrations

Some years ago Hancock (*11*) told the senior author that he had observed maxima in foam layer thickness as the salt concentrations in his experimental boiler were increased, and he suggested that it might be desirable to carry the concentrations in commercial boilers at or beyond the point of this maximum foam height. Hancock did not make a systematic study of the phenomenon, however, and since it is a matter of interest, such a study was included in this investigation. The water level and the rates of evaporation permitted pushing the concentrations of the synthetic boiler waters to over 100,000 p. p. m.; by so doing, maxima in foam heights were found in nearly all the salt solutions.

The measurements of foam heights in the boilers could not be made exact, but by taking the average of several readings at each concentration of boiler water, semiquantitative results were obtained. Two typical series of such results with sodium chloride solutions are shown in Figure 3.

Figure 3 indicates that the concentrations of salt used in the experiments were far above those occurring in commercial boilers, but it should be remembered that conditions were being pushed to extremes in order to find the maxima in foam height, if any existed. Perhaps it is of no practical value at present to know that these maxima were observed only at concentrations above those in commercial boilers. The authors can say, however, that their experiments satisfied their scientific curiosity. Future steam engineers may possibly find the information useful. It should, however, be pointed out that the curves conform to the fact that the rate of increase in the foaminess of a solution is much greater at the low than at the high concentrations. This is important for steam engineers to keep in mind.

In general the results of the experiments on foam height can be summarized as follows:

1. In the cylindrical boiler all of the salts showed maxima in the thickness of foam layer on their boiling solutions as the concentration was increased. On the solutions of sodium chloride and carbonate the foam thickness dropped at the higher concentrations. In the case of calcium and magnesium chloride solutions this falling off was not so marked.
2. In the water tube boiler the solutions of sodium sulfate and carbonate gave no indication of maxima at the concentrations used, but in both cases the increase in foam height was most rapid in the region of low concentration. Solutions of sodium chloride and sodium aluminate (a mixture of aluminate and hydroxide) showed distinct maxima with decidedly thinner foam layers at the high concentrations.

A decrease in foaminess at higher salt concentrations is to be expected on theoretical grounds, because in that region there is less difference in concentration between surface and mass of the solution than in more dilute solutions.

Mists or Fogs in Steam Space

Mists or fogs were observed in the steam space of both boilers. If distilled water was in the boiler, the mist was intermittent and appeared on the upstroke of the pump. This would be immediately after the introduction of cold water following the downstroke, and therefore the appearance of the mist was probably due to a momentary lowering of temperature and pressure. In the salt solutions the mist was always present. At one time, with distilled water in the boiler and at about 50 pounds pressure, there was a play of colors from yellow to red and then green. This color effect was evidently the result of changing size of the particles.

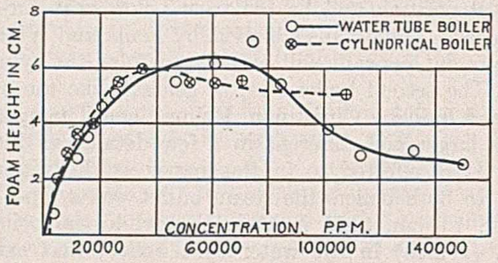

Figure 3. Effect of Sodium Chloride Concentration on Foam Height

Other investigators have also looked for such mists. Eberle (*3*) reports that he saw no fog (*Dampfwolken*) in the steam space with pure water in the boiler, but curiously enough he makes no mention of the appearance of the steam space over boiling salt solutions. Eberle's boiler had glass windows and operated at atmospheric pressure. Joseph and Hancock describe the appearance of the water and of the foam in their boiler but do not mention fogs or mists. J. A. Holmes in the discussion of a paper by Foulk (*6*) describes in the following words the appearance of the water and the steam in his experimental boiler: "When operating our experimental boiler, as the pressure increased to 450 pounds we could not see through the water, but could see through the steam by placing a light back of the sight glasses. Above 450 pounds there was a gradual clearing up of the water and a darkening of the steam, so that at 600 pounds pressure or above, we could see through the water easily but could not see through the steam, which had a very black appearance."

Stumper (*14*) states that it is impossible for water to be carried along in the steam in the form of minute droplets and that observations in suitable testing boilers show the absence of mists. He assumes that salt dusts resulting from the evaporation of droplets of boiler water are in the steam.

Apparently the presence of mist in the steam is determined by the experimental conditions. That the mists observed in the present investigation were not always salt dust is proved by their being present when distilled water was in the boiler.

No attempt at measuring the effect of these mists on carry-over was made. Such effect must, however, be very small.

Conclusions

The results of this investigation show that in every case gross carry-over was caused by foam that reached and covered the steam outlet. Since the two boilers differed so widely in design and were operated at different pressures, this fact seems significant and suggests that more emphasis should be put on the study of foaming conditions.

Since the maxima observed occurred at concentrations of dissolved salt above that in commercial boilers, no estimate of the practical value of this property of boiler water can be made at the present time.

Some observations are also recorded on the appearance of the foams on the boiler waters, and on the presence of mist or fog in the steam space in the boilers. No conclusions can be drawn from these observations, however, because no connection between them and the extent of carry-over could be noted.

The old question also comes up as to whether the behavior of the water in a commercial boiler is the same as that of the water in these experimental boilers, and again the old answer will be given. Only a long series of experiments with commercial boilers could determine whether the behaviors are the same, but it does not matter; because the main object of work with experimental boilers is to suggest new ideas to the operators of commercial boilers.

Acknowledgment

Grateful acknowledgment is made of the many courtesies of The Ohio State University Research Foundation, of The Ohio State University Engineering Experiment Station, and especially of the generous financial aid from the National Aluminate Corporation.

Literature Cited

(1) Cassidy, paper presented at joint meeting of the Engrs.' Soc. West. Pennsylvania and Pittsburgh Section of Am. Soc. Mech. Engrs., Pittsburgh, Oct. 15, 1935.

(2) Christman, Holmes, and Thompson, Ind. Eng. Chem., 23, 637 (1931).

(3) Eberle, *Arch. Wärmewirt.*, 10, 329 (1929).

(4) Foulk, Ind. Eng. Chem., 16, 1121 (1924).

(5) Foulk, *J. Am. Water Works Assoc.*, 17, 160 (1927).

(6) Foulk, *Trans. Am. Soc. Mech. Engrs.*, RP-54-5, 105 (1932).

(7) Foulk and Groves, Ind. Eng. Chem., 25, 800 (1933).

(8) Foulk and Miller, *Ibid.*, 23, 1283 (1931).

(9) Foulk and Ulmer, *Ibid.*, 30, 158 (1938).

(10) Foulk and Whirl, *Ibid.*, 26, 263 (1934).

(11) Hancock, personal communication.

(12) Jakob, Max, *Mech. Eng.*, 58, 643 (1936).

(13) Joseph and Hancock, *J. Soc. Chem. Ind.*, 46, 315T (1927).

(14) Stumper, *Wärme*, 59, 478 (1936).

(15) Ulmer, Ind. Eng. Chem., Anal. Ed., 9, 172 (1937).

Electrodeposition of Lubricants from Aqueous Dispersions

Electrodeposition is effective as a means of forming or depositing lubricant films on wire or other metallic surfaces. Whether or not enhanced lubricant results from electrodeposition depends largely on the physical nature of the deposited film.

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THE field of lubrication as applied to metal-forming operations affords examples where the application of relatively thick films of solid lubricants is advantageous (*1*). Thick films of lubricant are commonly applied to metal sheets, rods, or other shapes by spraying, brushing, or dipping preparatory to drawing.

The investigation of drawing lubricants for such forming operations also involved the study of various factors concerned with the use of soap solutions and fat emulsions (*2*). It was shown that adsorption, broadly, was responsible for the lubricating action of a soap solution when wire was drawn through a die immersed in or bathed by the solution. It appeared that film formation by adsorption of the dispersed lubricant phase might be aided by setting up an electric field where the wire would be the anode in the case of negatively charged lubricant "particles." A preliminary report on electrodeposition has already been published (*3*).

Apparatus and Procedure

Measurement of the pull on the wire-drawing die provided a means for the evaluation of the factors involved in lubrication as influenced by electrodeposition. The apparatus consisted of a glass tube, 11.4 × 2.2 cm., which was clamped horizontally against the die holder (Figure 1). The tube acted as an electrodeposition cell. The wire passed through the lubricant solution contained in the cell prior to being drawn through the die. A carbon electrode was inserted through the rubber stopper. The distance between the carbon electrode and the wire was 0.9 cm. Storage batteries supplied d. c. voltage up to 30 volts. A resistance placed in parallel provided a means for varying the voltage. Contact with the wire was made by clamping onto the steel dynamometer plate. An ammeter registered the current flow. The lowest current density calculated was of the order of 0.019 ampere per sq. cm. (0.003 ampere per square inch); the highest was 1.05 amperes per sq. cm. (0.16 ampere per square inch).

The polarity of the wire could be changed at will, depending upon the charge possessed by the dispersed lubricant. In the experiments reported here, the wire was the anode.

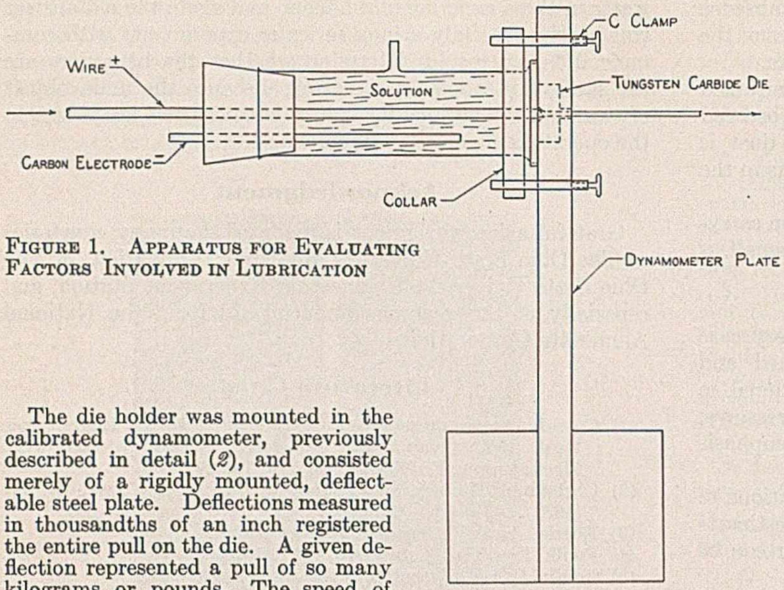

Figure 1. Apparatus for Evaluating Factors Involved in Lubrication

The die holder was mounted in the calibrated dynamometer, previously described in detail (*2*), and consisted merely of a rigidly mounted, deflectable steel plate. Deflections measured in thousandths of an inch registered the entire pull on the die. A given deflection represented a pull of so many kilograms or pounds. The speed of drawing was 30 cm. (approximately 1 foot) per minute, unless otherwise indicated. Die pull in these experiments was independent of the speed of drawing from 1 to 100 feet per minute. The back pull necessary to keep the wire taut was slightly less than one pound and was also kept constant in the experiments reported here. Fresh solutions were used for each reading, because the capacity of the cell was so small that impoverishment would result in prolonged runs. The percentage reduction in pull on the die refers to the ratio of the pull with the applied potential to the pull, using the lubricant bath with no potential applied. The percentage reduction would be much greater if the pull with the applied potential were compared to the pull with no lubricant.

Electrodeposited Films

The effect of the electrodeposition of lubricant from a 0.225 per cent solution of sodium soap with a pH of 9.5 (from fatty acid of 40.8 titer) on the drawing of 0.0253-inch soft copper wire, through a 0.0225-inch tungsten carbide die is shown in Table I.

Table I. Electrodeposition of Lubricant Films

Volts	Ampere	% Reduction in Pull on the Die
1.0	0.000	0
1.9	0.001	29
3.75	0.003	29
7.5	0.007 minus	33
15.0	0.013 plus	36
22.5	0.022	36
30.0	0.030–0.038	40

When the voltage was impressed sufficiently to cause an appreciable current to pass through the cell, a pronounced reduction in pull was effected. Simultaneous with current flow, a greenish coating, visible to the naked eye, was deposited on the wire. At higher voltages the pull on the die decreased further.

It is believed that the lubricating film, deposited on the wire in these experiments and primarily responsible for the enhanced lubrication, was copper soap formed by the union of the fatty acid radical ions and copper ions from the wire. In the earlier paper (*1*) dealing with waxlike lubricants, copper oleate was also effective; it was pointed out that three conditions relative to the unusual effectiveness of wire drawing lubricants must be satisfied: (*a*) The lubricant must adhere strongly to at least one of the surfaces—the wire or the die; (*b*) the lubricant must be solid prior to being subjected to the relative shearing of the surfaces to be lubricated; (*c*) the lubricant must melt or be transformed to a fairly mobile liquid between the surfaces while shearing takes place. Copper soap made from a fatty acid of 40.8 titer satisfies these conditions.

The above experiments were repeated but the pH of the 0.225 per cent sodium soap solution was varied by adding hydrochloric acid to decrease it and sodium hydroxide to raise it. These results are shown in Table II.

It is not difficult to explain the rather remarkable results in Table II on the basis of previous work done on the admixing of fatty acids and copper oleate where the waxlike copper oleate lost adhesion and consequently enhanced lubrication was not obtained. In fact, precipitated copper oleate heated to 100° C. for 15 minutes decomposed to form sufficient fatty acid to prevent good adhesion of the copper oleate to the wire. The sweating out of an oily phase from an otherwise waxy solid does not permit enhanced lubrication, since adhesion to the wire is lost.

In the experiments (Table II) it is believed that simultaneous deposition of fatty acid as such (by electrophoresis) at the lower pH values likewise adversely affects lubrication by the copper soap. At pH 11.8 the evolution of oxygen gas at the wire, as a result of relatively high hydroxyl ion concentration, caused a disruption of the film of copper soap and probably accounted for erratic results.

The study of the effect of pH on the lubricating effectiveness of soap solutions (*2*) showed a gradual decline in lubricating effectiveness as the pH was raised to the vicinity of pH 12; at this point there was a sharp decline which resulted in no lubrication whatsoever as the pH was still further increased. As pH was increased, in these experiments, there was a beneficial effect until gassing (oxygen) was pronounced. This would be expected with the repression of hydrolysis as pH was increased and a consequent reduction in free fatty acid. No substantial effect on the repression of ionization of the sodium soap was experienced, judging by the deposition of copper soap which presumably requires the existence of fatty acid radical ions.

As a control experiment a sodium hydroxide solution of pH 12 was electrolyzed. The wire was drawn with great difficulty, seizure occurring spasmodically.

Table II. Effect of pH on Lubrication by Soap Solution Subjected to Electrodeposition

Volts	% Reduction in Pull on Die			
	pH 7.5	pH 9.5	pH 10.2	pH 11.8
1.0	6	0	..	..
1.9	8	29	17	17
3.75	10	29	30	41
7.5	10[a]	33	46	44
15.0	10[a]	36	46	44
22.5	..	38	46[a]	44
30.0	0	40	46[a]	44[a]

[a] Erratic.

Table III. Effect on Lubrication of the Electrodeposition of Beeswax from Emulsion Containing 0.9 Per Cent Wax and 0.15 Per Cent Sodium Soap (pH 9 Plus)[a]

Volts	Ampere	% Reduction in Pull on Die
1.9	0.001	35
3.75	0.004	37
7.5	0.009	39
15.0	0.024	40
30.0	0.054	36

[a] All tests drawing 0.0253-inch soft copper wire.

Table III presents the results with a beeswax emulsion in the cell.

Favorable reductions in pull were observed. When 15 volts were used, the actual pull in pounds was the lowest observed in any experiment reported here. Beeswax was the most effective waxlike lubricant tried under the similar conditions reported previously (*1*). Unlike fatty acid which was also simultaneously deposited (Table II), beeswax augmented efficiency because of its adhesive nature and typical waxy properties. Beeswax stably emulsified with soap is not particularly effective in reducing die pull. It is apparently not adsorbed readily. Electrodeposition of tallow from an emulsion containing 1.4 per cent tallow and 0.2 per cent potassium soap (pH 8.6 to 10) gave no enhanced effect under conditions identical to those in Table I. Here, as in the case of the soap solution containing appreciable quantities of free fatty acid, the waxlike nature of the copper soap was changed by the tallow. A rather heavy coating of tallow admixed with the greenish copper soap was readily observed, however. Emulsions of tallow in soap solutions have never shown any advantage over soap solutions alone in this experimental device without the electrodeposition procedure.

With 0.1 per cent sodium stearate (pH 9.9) no enhanced lubrication was observed and no visible deposition of green copper soap was noted at room temperature when currents up to 30 volts were used. When the temperature of the solution was raised to 75° C. so that the sodium stearate "dissolved" and subsequently ionized, enhanced lubrication did result and copper stearate was formed in visible quantities.

Regarding the time required to deposit an effective film from a soap solution such as is described in Table I, 0.1 second is sufficient. Thus commercial drawing speeds should offer no particular difficulty, if we take into consideration an electrodeposition "cell" of reasonable size. The original electrodeposited film is carried through three to four dies with a measurable lessening of die pull.

Literature Cited

(1) Williams, R. C., Ind. Eng. Chem., 27, 64 (1935).
(2) Williams, R. C., *J. Phys. Chem.*, 36, 3108 (1932).
(3) Williams, R. C., *Wire & Wire Products*, 12, 754 (1937).

Reaction of Carbonic Acid with the Zeolite in a Water Softener

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SINCE the commercial introduction of the zeolite method or base exchange of water softening, it has usually been considered that the only exchange reactions occurring were those involving the basic ions. Although Riedel (*2*) in 1909 described the reaction of dissolved carbon dioxide on zeolites, comparatively little consideration has been given to the basic properties of the hydrogen ion. In this paper we show, as softening proceeds, that there is a gradual decrease in alkalinity with the formation of hydrogen zeolite, which subsequently exchanges its hydrogen ion with basic ions and thus forms free carbon dioxide and lowers the pH of the effluent water.

Two stations of the Panhandle Power and Light Company are supplied by deep well water having an analysis similar to that shown in Table I. The only significant difference is that the water at Jowett Station, near Mobeetie, Texas, contains 15 p. p. m. of carbon dioxide, whereas the water used at Riverview Station, near Borger, Texas, contains 7 p. p. m.

Table I. Analysis of Well Water at Jowett Station

	P. p. m.	*Grains/gal.*
Total solids at 103° C.	319	18.7
Total hardness as $CaCO_3$	206	12.0
Total alkalinity	190	11.1
Silica	24.8	1.45
Fe_2O_3 and Al_2O_3	1.2	0.07
Calcium	73.0	4.27
Magnesium	6.0	0.35
Sodium	26.2	1.53
Bicarbonate	232.0	13.55
Carbonate	0.0	0.00
Chloride	18.0	1.05
Sulfate	33.0	1.93
Nitrate	17.7	1.03
Carbon dioxide	15.0	0.88

Because of the low sulfate-carbonate ratio the boiler feed water was treated at Jowett Station with sulfuric acid prior to softening, and at Riverview Station with acid following the softening. The total alkalinity of the water was reduced from 190 to 25 ± 5 p. p. m. At Jowett Station it was observed that no matter how narrow the range of alkalinity in the influent to the softener, there was always a wide variation in the total alkalinity of the effluent.

Cause of Variation in Alkalinity of Effluent

An investigation was made to determine the extent and the cause of these variations. The usual methods of operating the water softener were followed. The total alkalinity of the influent and effluent during the softening period is shown in Figures 1 and 2. In the beginning the total alkalinity of the effluent was much higher than that of the influent but gradually decreased as the softener became exhausted, until it was less than that of the influent.

In following the idea that dissolved carbon dioxide in the water might be responsible for the observed changes, tests were made in which the quantity of free carbon dioxide was compared to the total alkalinity in the influent and effluent waters. Typical data from one of these tests are shown in Figure 1. The influent was untreated Jowett Station water with a free carbon dioxide content of 15 p. p. m. Similar data are shown in Figure 2 when using Riverview Station water which contains 7 p. p. m. of free carbon dioxide.

During the initial portion of the run, free carbon dioxide was absent in both cases. From the point at which free carbon dioxide began to appear until the end of the run, the carbon dioxide content increased gradually, and in the latter portion of the run it occurred in greater quantities than in the influent.

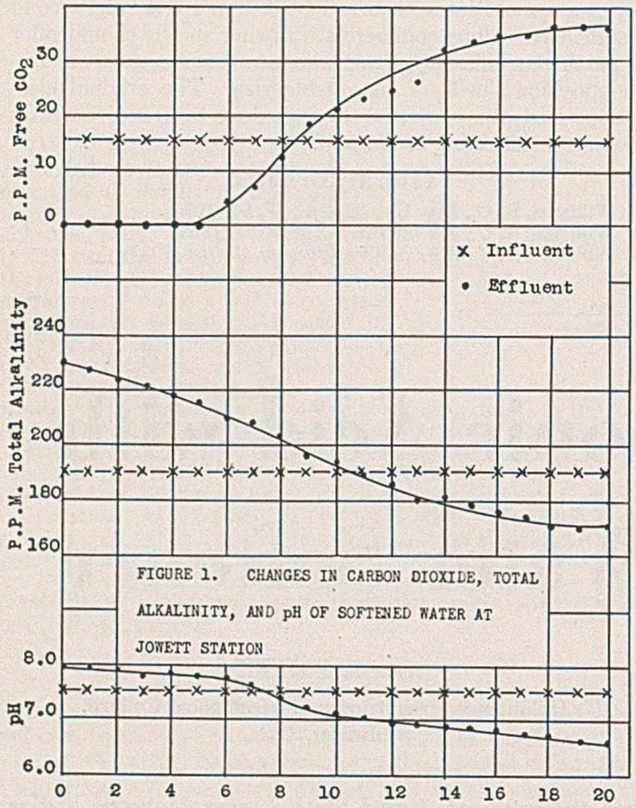

FIGURE 1. CHANGES IN CARBON DIOXIDE, TOTAL ALKALINITY, AND pH OF SOFTENED WATER AT JOWETT STATION

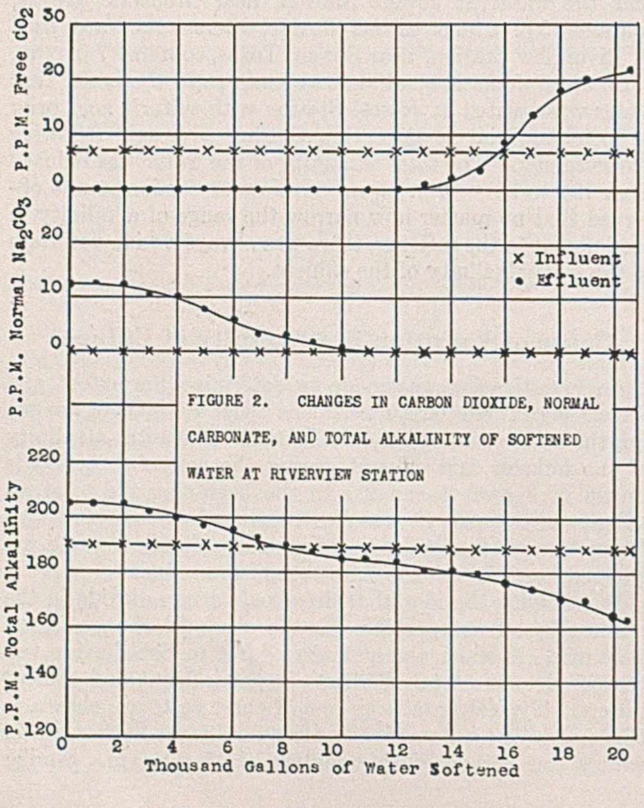

FIGURE 2. CHANGES IN CARBON DIOXIDE, NORMAL CARBONATE, AND TOTAL ALKALINITY OF SOFTENED WATER AT RIVERVIEW STATION

This is evidence that the quantity of free carbon dioxide in the effluent is linked to the changes in alkalinity and that probably this carbon dioxide is the result of the reactions taking place in the zeolite bed. The assumption of the formation of hydrogen zeolite now seems quite logical.

It is believed that the reaction which occurs between carbonic acid and sodium zeolite results in the formation of hydrogen zeolite and normal carbonate. When the quantity of free carbon dioxide in the influent is around 7 p. p. m., the increase in alkalinity which occurs in the early part of the softening run appears to be due to the formation of normal carbonate (Figure 2). However, if the free carbon dioxide content of the influent water is around 15 p. p. m. or higher, then normal carbonate does not appear in the effluent but instead the observed increase in total alkalinity appears to be due to the bicarbonate ion (Figure 1).

The probable subsequent reaction of hydrogen zeolite also may explain the decrease in the total alkalinity of the effluent below that of the influent during the latter stages of softening, and the increase in the quantity of free carbon dioxide during this stage.

Zeolite Reactions

As softening progresses, there is a decrease in the quantity of sodium zeolite remaining in the zeolite bed and a corresponding increase in the quantity of calcium, magnesium, and hydrogen zeolite. Finally, a limiting point is reached at which the ability of the sodium zeolite to exchange completely with the hydrogen ion is exceeded. After this point is passed, there is an exchange reaction between the hydrogen zeolite and the calcium and magnesium ions entering the softener. This reaction would yield a hydrogen ion and either calcium or magnesium zeolite, and thus lower the total alkalinity and pH and form free carbon dioxide. Other workers (*1*) in this field observed the pH variation which occurs throughout the softening cycle and also suggested the possibility of hydrogen zeolite formation.

The following experiments were made to check these assumptions. Carbon dioxide gas was passed through distilled water until the pH of the water was 6.8. The water was then allowed to percolate through a small quantity of greensand zeolite. The effluent had a pH of 9.0 and contained only carbonate alkalinity to the extent of 21 p. p. m. as sodium carbonate. Carbon dioxide gas was further passed through distilled water until the pH of the water was lowered to 4.9. When this water was allowed to percolate through the zeolite bed, the pH increased to 7.9 and only bicarbonate alkalinity appeared to the amount of 110 p. p. m. as sodium carbonate. Then when sufficient carbonated distilled water had been passed through the zeolite bed so that no further change occurred, tap water of a pH of 7.5 and a total alkalinity of 190 p. p. m. was substituted for the carbonated water. The effluent water had a pH of 4.4 after it had been heated and aerated to drive off any carbon dioxide; the formation of hydrogen ions was thus indicated.

This procedure also indicates that carbonic acid occurring in water is probably responsible for the observed changes which occur in the total alkalinity, pH, and dissolved carbon dioxide content of the effluent of a zeolite softener. Any hydrogen ion could form hydrogen zeolite by reaction with the sodium zeolite, but under normal operating conditions the formation of hydrogen zeolite is dependent only on the presence of carbonic acid in the influent.

Literature Cited

(1) Behrman, A. S., and Gustafson, H., IND. ENG. CHEM., 28, 1279–82 (1936).
(2) Riedel, J. D., German Patent 224,934 (Nov. 23, 1909).

PRESENTED at the 95th Meeting of the American Chemical Society, Dallas, Texas.

Leafing of Aluminum Pigments

The literature contains a variety of qualitative observations on the leafing of aluminum pigment. Quantitative information, however, depends on precise methods of measurement. This paper presents a study of the factors involved in the measurement of leafing by the so-called spatula method. This information permits an intelligent adaptation of the leafing test to particular problems and also helps in the interpretation of leafing measurements. There is also included a variety of observations on the effect of various factors on the leafing of aluminum pigment under different conditions of application. It is hoped that this discussion will lead to a better understanding of leafing and methods for its measurement.

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THE leafing of aluminum flakes in aluminum paint is a phenomenon with which all users are familiar in a general way. A precise understanding of leafing, however, must depend upon quantitative measurements of the effect.

When flake aluminum pigment is stirred in a varnish vehicle, the flakes swirl around, and the motion of the liquid brings some of the flakes to the surface. If their characteristics are right, many of these flakes will stay at the surface when stirring slows up or ceases, and form what appears to be a continuous film of metal. This is the leafed film; its formation is a complex function of certain properties of the aluminum flakes and the vehicle in which they are immersed, as well as other factors, some of which are known. This action of leafing also occurs when aluminum paint is brushed or sprayed on a surface. Under these conditions of practical usage, leafing is even more striking and more complete because the paint film is comparatively thin and every flake is nearer to the free surface and hence has a better chance of leafing.

Not only the existence of the leafed layer at the surface of the vehicle can be demonstrated by the examination of cross sections of aluminum paint films under the microscope, but also the layerlike distribution of the remaining flakes throughout the paint film is clearly shown. In Figure 1, a cross section of an aluminum paint film, the leafed layer is a thin line of flakes at the top of the paint film. The remaining flakes are roughly disposed so that their broad faces are approximately parallel to the surface to which the paint has been applied, and they are therefore viewed "on edge" in the cross section. In a strictly technical sense the term "leafing" applies only to the thin layer of flakes just at the surface of the vehicle; however, since the other flakes in the paint film remain disposed in much the same manner as a pile of fallen leaves, the term "leafing" has from time to time been descriptively applied to the arrangement of all of the aluminum flakes in the paint film.

A simple method sometimes employed for determining whether aluminum powder has the quality of leafing is to stir the powder with a suitable vehicle in a small dish such as an evaporating dish. After the mixture has stood for a given period after cessation of stirring, an observation is made as to whether or not the entire surface of the liquid is covered with a leafed film of aluminum flakes (*4*). As a quantitative procedure the method has obvious disadvantages; furthermore, it does not work satisfactorily with aluminum paste pigments.

In making such a test, however, a number of important phenomena can be observed, which must be taken into consideration in any method of evaluating leafing. While the mixture of aluminum paste or powder and vehicle is being stirred, the flakes can be seen swirling around in the fluid currents produced by stirring. It is these currents which bring flakes to the surface and help the powder to leaf. Evaporation of solvent also assists in producing convection currents in the paint mixture, as does the liberation of small bubbles of air admixed with powder. Blowing gently upon the surface of the paint also results in an increased tendency to leaf. If a brushful of the paint is wiped against the vessel so that the paint flows down the side in a thin film, leafing will readily occur in this thin-moving film and spread out over the main surface of the paint.

Leafing is a combination effect of pigment and vehicle. In the case of the pigment, the size and shape of the aluminum flakes are factors in determining their ability to leaf, as is also their surface condition. In the manufacture of aluminum powder, the surface of each flake is coated with a thin film of stearic acid or similar material, the molecules of which are probably oriented to a substantial degree. This orientation or arrangement of the long polar molecules of stearic acid so that the carboxyl groups are similarly directed makes an important change in the surface forces of the aluminum flakes. The surface tension relations between this oriented film and the vehicle are factors in determining the degree of leafing observed in any case. Because of the forces of surface tension, the leafed flakes stay at the surface and do not sink, although

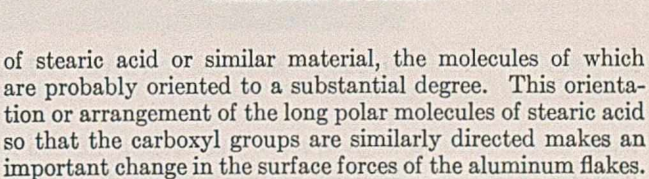

FIGURE 1. CROSS SECTION OF ALUMINUM PAINT FILM

Thickness of paint film indicated at *A*; arrow at *B* points to leafed flakes at surface they are specifically denser than the fluid in which they are immersed. In general, the vehicles with the higher surface tensions have the best leafing properties (*5*).

Spatula Leafing Test

A test which provides a numerical value for leafing has been in use in the Aluminum Research Laboratories for a long time (*1*, *2*).

A standardized steel spatula is dipped into a well-stirred mixture of aluminum paste or powder with a vehicle. It is then withdrawn and suspended vertically; after a specified interval of time, the film is examined and a measurement made of the proportion of the total immersed area which is completely leafed. The leafing value is expressed as a percentage.

The test vehicle or "leafing liquid" consists of a solution of 30 grams of powdered hard coumarone resin (melting point, 127–142° C.) in 100 cc. of mineral spirits meeting Federal Specification TT-T-291. The blade of the spatula is 14 cm. long and 1.4 cm. wide. In making the test, a predetermined weight of aluminum pigment is stirred into 25 cc. of the leafing liquid, and the well-mixed paint, at 20–30° C., is poured into a test tube 2 cm. in diameter. The spatula is dipped at once into the freshly mixed paint until it touches the bottom of the test tube. The spatula is then withdrawn without touching the side of the test tube and suspended vertically in free space for 3 minutes. The height of the perfectly leafed area is then measured and expressed as a percentage of the total depth of immersion of the spatula.

Before proceeding to an analysis of the variables which affect this test, it is worth while to consider just what happens during the test. When the spatula is withdrawn from the paint container, a film of paint adheres to the surface of the spatula. Certain forces are at work to promote leafing in this film, and certain forces oppose. Motion of the aluminum flakes within the paint mixture is necessary to bring them to the surface. Because the paint film is thin, the flakes do not have far to go to reach the surface. Motion is provided in part by the tendency of the paint mixture to flow down the spatula; evaporation of the solvent also aids in producing movement of the flakes. When an aluminum flake has once leafed, the forces of surface tension, if strong enough, hold it at the surface. However, the same currents which brought the flake to the surface may take it away again if the force of surface tension is not great enough to hold it against them.

Another force opposing leafing arises from the viscosity of the vehicle. The more viscous the vehicle, the greater the resistance to movement of the flakes within it. The initial viscosity of the vehicle will have an effect upon the rate of leafing and perhaps on the completeness; furthermore, the viscosity will increase as the solvent evaporates and the vehicle dries, so that eventually it will become great enough to prevent any movement of the flakes or liquid and hence put an end to leafing.

The best leafing flakes remain at the surface and collect in little groups or islands which are pulled down the vertical surface of the spatula by gravity and build up a continuous leafed area beginning at the bottom of the spatula. Here some of these flakes are lost in the drop or two of liquid which almost invariably falls from the spatula.

The leafed area increases as long as there are leafable flakes in motion and a place in the surface of the film for them to occupy. The time element must therefore be considered in this test. For example, a slow-drying vehicle of relatively high viscosity often shows a greater leafing value by the spatula method than is exhibited by the same pigment in a thin, fast-drying vehicle such as the leafing liquid. However, the time required will be much longer.

Effect of Pigment Concentration

The leafing test is not an exact measure of the number of flakes which are capable of leafing. Many flakes which would otherwise leaf never reach the surface; many more arrive too late and find their places occupied by other flakes, so that although they are theoretically able to leaf, the observer never becomes aware of that fact. Some of these flakes become entrapped behind the leafed film and account for the roughness observed on the lower part of the spatula when the film dries (Figure 2).

The leafing values obtained when increasing quantities of powder are used are given in Table I, and the appearance

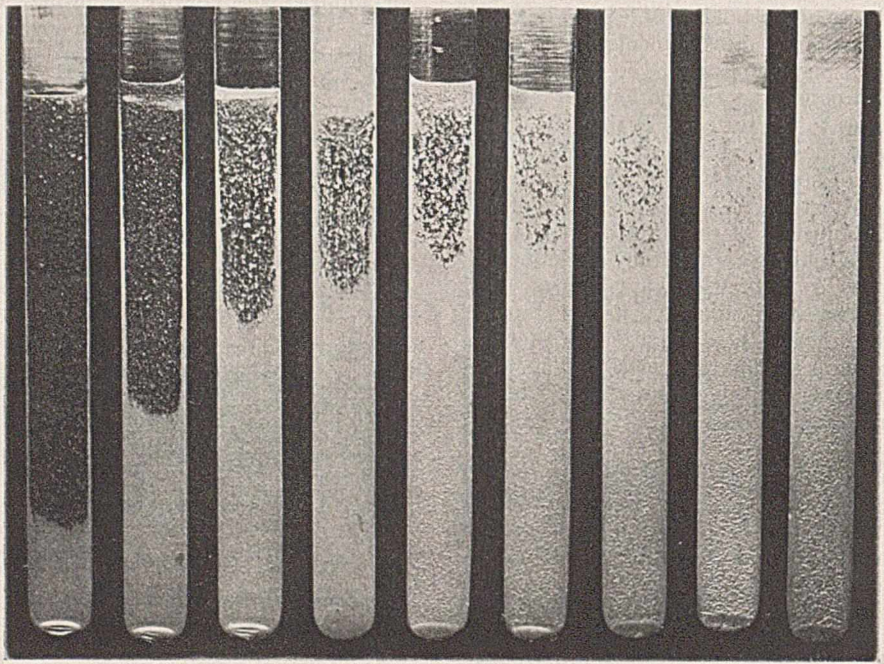

Figure 2. Spatulas Employed in Leafing Test, Showing (from Left to Right) the Effect of Increasing Concentrations of Pigment in the Leafing Liquid

of a corresponding group of spatula tests is shown in Figure 2. With the lower concentrations of powder the measured leaf is roughly proportional to the amount of powder taken; above a certain point it increases more slowly and finally reaches a constant. In some cases the use of high amounts of pigment results in a spatula completely filled in and marked PC (practically complete), as will be explained later.

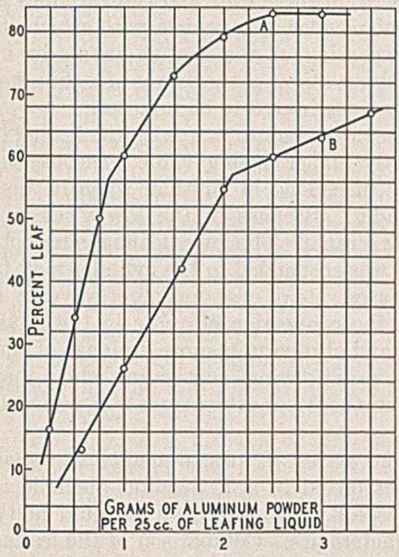

FIGURE 3. RELATION BETWEEN PER CENT LEAF IN SPATULA TEST AND CONCENTRATION OF PIGMENT IN LEAFING LIQUID

A, pigment of high covering area; *B*, of low covering area

This proportionality between the percentage of pigment and the percentage of leafing suggests that another comparison be made between the area of the aluminum flakes and the leafing percentage. Fortunately, it is a simple matter to determine the surface or covering area of the flakes by the method of Edwards and Mason (*3*). This is accomplished by sifting a weighed sample of powder upon a water surface held in a rectangular container. The powder is not wet by the water and leafs upon its surface. The powder is then manipulated back and forth by two glass barriers so as to stretch it out to a continuous film one flake thick. The area covered by the flakes when closely packed and touching can then be measured directly. This is the maximum area which the sample of powder can cover by leafing. With a determination of the weight of powder retained on the spatula, it is possible to calculate the covering area of the aluminum flakes on the spatula and hence of the maximum leafed area which they can produce if they all leaf.

TABLE I. EFFECT OF ALUMINUM POWDER CONCENTRATION ON LEAFING VALUE

Standard Powder	Per Cent Leaf for Following Concns. of Powder, in Grams/25 Cc. of Leafing Liquid:						
	0.5	1.0	1.5	2.0	2.5	3.0	3.5
Lining	34	60	73	79	83	83	PC[a]
Varnish	12	26	40	55	60	63	67

[a] Practically complete leaf.

The two graphs of Figure 3 show the relation between the observed percentage of leafing in the spatula test and the concentration of powder in the paint mixture. These graphs were made with two different powders of high and low covering area. The relation between leafing and pigment concentration is a straight-line function up to a certain point on each of these graphs. For many powders at the point where the break occurs (that is, where the relation departs from one of direct proportionality) the area of all the flakes on the spatula is just about sufficient to cover completely the immersed area, provided all the flakes leaf. Too much physical significance should not be attached to this relation, however, since there are appreciable deviations.

Although the covering area of a paste or powder has no connection with the intrinsic leafing ability of the aluminum flakes, it may have an important effect upon the observed area of leafing in the spatula test, as Figure 3 shows. The relation between covering area and leafing power is shown in a somewhat different way in Figure 4. The percentage of leaf observed in a large number of tests is plotted as a function of the available flake area. The term "available flake area" is used to describe the total covering area of the aluminum flakes actually on the spatula in each test. This value is calculated from a knowledge of the covering area of pigment employed, the concentration present in the paint mixture, and a determination of the amount of paint carried on the spatula in each test. The vertical dotted line, corresponding to an area of about 30 sq. cm., gives the immersed area of the spatula used in the test. Figure 4 indicates that the leafing power with these particular pigments is roughly proportional to the available flake area up to a critical point, which is approximately that of the immersed area of the spatula; beyond this point the leafing power shows irregular but minor changes with increase in available flake area. Some of the pigments show a leafing power which is very close to that of the theoretically perfect leaf, but none can exceed the perfect leafing value.

It is not possible to get every flake into the surface of the vehicle on the leafing spatula because of the formation of a film of leafed flakes which traps other flakes behind it. Furthermore, with pigments of inferior leafing power, not all of the flakes which reach the surface will remain there. If the spatula were suspended horizontally instead of vertically, all the flakes of a satisfactory leafing power would have a good chance to leaf, and perfect leaf should result. Since it is hung vertically, the leaf approaches perfection only with the combination of a heavy overload of pigment and a slow-drying vehicle of high viscosity which will hold the flakes in the upper part of the spatula in sufficient quantity to fill in at the top as fast as the flakes leaf at the surface and slide down towards the bottom.

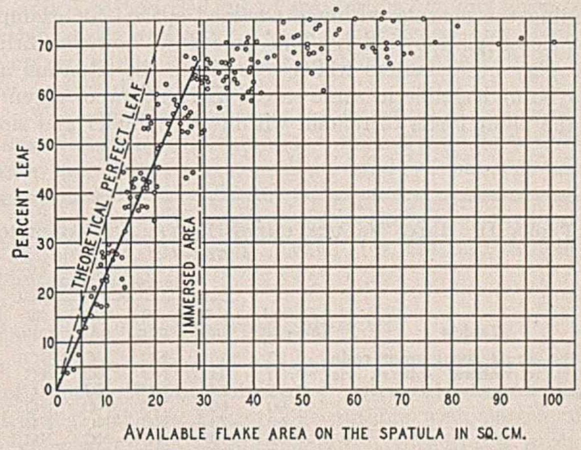

FIGURE 4. RELATION BETWEEN PER CENT LEAF IN SPATULA TEST AND TOTAL AVAILABLE FLAKE AREA OF PIGMENT ON THE SPATULA

Vertical dotted line shows the immersed area of the spatula

The term "practically complete leaf" is used in Table I to describe the condition illustrated on the two spatulas at the right of Figure 2. A completely leafed area appears below with an area near the top with very small breaks in an otherwise well-leafed surface. Where the quantity of leafable flakes is too large to spread over the area available on the spatula, the lower portion of the spatula becomes leafed and filled in behind the leafed surface so that any nonleafing flakes above are blocked from slipping behind the leafed area as would ordinarily occur. Also, as the liquid drains away and dries, other flakes are trapped above the leafed area where they more or less completely hide the spatula. The remedy is obviously the use of a smaller quantity of pigment, since above a certain point any additional amount only tends to produce this result and to obscure the limits of the truly leafed area.

Test Conditions

The spatula test obviously does not measure any intrinsic property of the flakes but is a measure of their behavior when mixed with a vehicle and exposed as a thin film to drying under certain conditions. Although these conditions may be selected arbitrarily, nevertheless a thorough knowledge of the factors affecting the test is important in order to select test conditions which permit readily reproducible results to be obtained and which give a reliable comparison between aluminum pigments.

It has already been stated that blowing on a mobile aluminum paint surface will facilitate leafing. Similarly, the presence of air currents around the suspended spatula bearing a wet paint film may have an effect upon the amount of leafing secured upon the spatula. Sometimes a difference in the degree of leaf on the two sides of the spatula may be attributed to the impingement of an appreciable air current upon one side. In general, air currents are not controllable, and to secure reproducible results the spatula should be suspended in still air.

This suggests that there might be an advantage in suspending the spatula within a confined space—for example, in a closed glass cylinder. This procedure, however, brings into play other factors which complicate the situation and may be undesirable in some cases. Solvent vapor given off by the paint tends to remain within the cylinder and slows up further evaporation of solvent from the paint film and hence affects the rate of setting and drying. The effect may, moreover, vary considerably, depending upon the composition of the vehicle with which the aluminum pigment is mixed. Table II gives data on the observed leafing on the spatula when it is hung freely in the air and when it is suspended in a confined space, in this case a glass cylinder of 3.8 cm. internal diameter and about 20 cm. high. The same powder was used for all of these tests and the variables were the concentration of powder, the vehicle with which it was mixed, and the suspension of the spatula in air or in the closed cylinder. Observations of the degree of leafing were also made at various periods from 3 to 30 minutes.

In the case of the paint made with the leafing liquid (Table II), a slightly higher leafing value was observed when the spatula was suspended in air than when it was placed in a closed cylinder. Because of the low viscosity of this vehicle, leafing is rapid. The lower leafing values obtained when the spatula was suspended in the cylinder may be attributed to the decreased rate of evaporation of solvent; this causes a decrease in the convection currents in the fluid mixture on the spatula and also permits more drainage of the paint. Because of the rapid drying, any leafing which may take place occurs within the 3-minute observation period used for this test.

The second series of measurements was made with the same powder mixed in a 12.5-gallon phenolic resin varnish of higher viscosity than the leafing liquid and with rapid-drying characteristics. Comparison of the leafing values observed after periods of 10 minutes or longer shows that the higher values are obtained when the spatula is suspended within the cylinder. This is particularly true in the case of the paint mixtures containing the higher concentrations of powder, and it appears probable that the accumulation of solvent vapor in the cylinder slows down the setting time of the paint mixture, so that the leafable flakes are given more time to leaf. Also the high viscosity of the vehicle reduces the number of flakes which slip down behind the leafed area and hence increases the number of available flakes above, where leafing is still possible at unfilled surface areas. In general, however, lower leafing values are obtained than with the leafing liquid because the higher viscosity of the vehicle slows down the rate so much that less leafing occurs before the paint mixture has set.

In the third series of tests, with the 50-gallon coumarone resin varnish, the vehicle was also of increased viscosity but it dried very slowly. After a sufficient time, therefore—for example, 30 minutes—very high leafing values are observed even with some of the lower concentrations of pigment. The results in the cylinder are lower than in the air, presumably because the decreased rate of solvent evaporation produces less motion of the flakes in the paint film on the spatula and permits more drainage.

If a few drops of a very volatile solvent, such as ether, are placed in the bottom of the glass cylinder, the paint film will not set at all but will simply run off the bottom end of the spatula, and no leafing whatever will be observed. A slow-drying vehicle suspended in a closed cylinder may also permit more paint to drop off the end of the spatula and hence lower the apparent percentage of leafing.

TABLE II. LEAF VALUES UNDER DIFFERENT CONDITIONS OF VISCOSITY AND DRYING RATE

Vehicle	Sample Weight[a]	Spatula in Air[b]				Spatula in Closed Cylinder[b]			
		3 min.	10 min.	20 min.	30 min.	3 min.	10 min.	20 min.	30 min.
Leafing liquid (coumarone resin, 30% in mineral spirits), viscosity 0.07 poise, fast drying	0.25	16	NC	NC	NC	15	NC	NC	NC
	0.50	34	NC	NC	NC	28	NC	NC	NC
	0.75	50	NC	NC	NC	43	NC	NC	NC
	1.00	60	NC	NC	NC	55	NC	NC	NC
	1.50	73+	NC	NC	NC	68	NC	NC	NC
	2.00	79+	NC	NC	NC	77+	NC	NC	NC
	2.50	83+	NC	NC	NC	83+	NC	NC	NC
	3.00	83+	NC	NC	NC	84+	NC	NC	NC
12.5-gal. phenolic resin varnish, viscosity 1.3 poises (tube E+), rapid drying	0.25	8+	12	NC	NC	..	15	NC	NC
	0.50	28+	31	NC	NC	23+	30	NC	NC
	0.75	39+	44+	NC	NC	26+	43	NC	NC
	1.00	37+	50+	NC	NC	26+	44	NC	NC
	1.50	40+	45+	NC	NC	36+	63	NC	NC
	2.00	40+	40+	NC	NC	38+	63+	71	NC
	2.50	42+	42+	NC	NC	42+	64+	75	NC
50 gal. coumarone resin varnish, viscosity 1.25 poises (tube E), slow drying	0.25	13+	19+	20+	21+	7+	12+	17+	18
	0.50	26+	53+	53+	53+	15+	31+	37+	40
	0.75	43+	64+	66+	68+	25+	43+	53+	57+
	1.00	58+	77+	88+	PC	35+	59+	69+	72+
	1.50	56+	75+	85+	85+	37+	66+	76+	79+

[a] Indicated weight in grams per 25 cc. of the vehicle; same Standard Lining-grade powder used throughout.

[b] NC = no change; PC = practically complete leaf; + indicates an appreciable amount of powder above the first break in the leafed area, which is unable to join the leafed area because of lack of time or rapid film setting.

Within reasonable limits the depth to which the spatula is immersed does not seem to be a factor in the observed percentage leaf. Four tests, with depths of immersion varying from 7 to 13 cm., showed the same percentage of leaf within the limits of experimental variation. It is convenient to use a 10-cm. depth of immersion so that the percentage leaf can be measured directly by means of a millimeter scale.

The shape and surface of the spatula used have some influence on the results obtained. The spatula should preferably have parallel sides with a rounded bottom. Tests have shown that a clean, polished stainless steel blade will give better reproducibility of results than other surfaces. If the surface is rough it will tend to hold more paint and be more subject to change with use than would otherwise be the case.

The proportion of pigment to be mixed with the leafing liquid will depend upon a number of factors. For investigational purposes, it is usually desirable to test a number of concentrations, so that a graph can be plotted to show the relation between leafing power and pigment concentration. The covering area of the pigment should also be measured to aid in the interpretation of the graph.

The spatula test is not now suggested as a method for inclusion in specifications; however, it is frequently informative to make preliminary comparisons of the leafing characteristics of unknown pigments, using arbitrary pigment concentrations. In comparing the leafing characteristics of Varnish grades of aluminum powder, the use of 2 grams of powder per 25 cc. of leafing liquid gives reproducible results. Where lining grades of powder are to be compared, the use of 1.25 grams per 25 cc. of leafing liquid is suggested. Where the pigment being tested is paste, an extra amount must be taken to allow for the volatile content of the paste; for example, with a paste of about 65 per cent metal content, a sample weight of 2 grams of Standard or Extra Fine Lining paste may be employed to give the 1.25 grams of aluminum pigment suggested. In reporting the percentage leaf, the grade of pigment and the weight taken for the test should be reported. Using the same sample weight for all pigments of the same grade will favor the pigment of higher covering area, other factors being equal. This is an advantage, but the pigment would have it in application and so might be justified on that score.

Again it should be emphasized that the test conditions are arbitrary and that even though the numerical leafing value by the spatula test appears low, the pigment may give practically perfect leafing under the conditions of practical application. The amount of pigment used with a vehicle in practice, however, is roughly three times as much as suggested above for the spatula test. For example, Standard Varnish, Standard Lining, and Extra Fine Lining powders are commonly mixed in the proportions of 2, 1.25, and 0.75 pound per gallon of vehicle, respectively, corresponding to 6, 3.75, and 2.25 grams per 25 cc. of vehicle (*6*).

Test for Leafing Power of Vehicles

The percentage leaf in the spatula test is a combination effect of both pigment and vehicle. The emphasis in this paper so far has been on the selection of test conditions which would permit a reliable comparison of the leafing power of aluminum pigments. By the use of a standard sample, preferably powder of the Extra Fine Varnish grade, it is also possible to employ the spatula test to compare the leafing power of various vehicles.

The first point to be considered is the amount of powder which should be mixed with the vehicle. For some types of comparison it would seem desirable that the paint retained on the spatula should contain the same weight of powder in each case, so that there would be the same flake area available for leafing. Since, however, the spatula will take up more paint with the vehicles of higher viscosity, it is necessary to adjust the concentration of powder in the vehicle to take account of this factor. This detail complicates the test, but it is possible to determine by preliminary experiments the relation between the viscosity of the vehicle and the powder concentration required to give the same amount of powder on the spatula in each test.

For most purposes it would not seem necessary to introduce this refinement into the test, since the use of some standard amount—say 1 gram of powder (with a covering area of about 6000 sq. cm. per gram) to 25 cc. of liquid—rates the leafing power of vehicles in approximately the same order as is observed in their practical application. If the vehicle of higher viscosity carries a little more powder onto the spatula, it is also true that it is likely to give a thicker paint film when applied in a practical way.

When determining the leaf of an aluminum paint made with an oleoresinous vehicle, bubbles are sometimes present on the leafing spatula even when the greatest care is exercised. The presence of these bubbles in the paint film tends to change the observed leafing value. The test should be repeated carefully to avoid the formation of bubbles.

Summary

1. A numerical value for the leafing of aluminum pigments can be obtained by dipping a spatula into a mixture of the pigment and a special leafing liquid, withdrawing the spatula, suspending it in free air, and measuring the percentage of leafed area after 3 minutes.

2. The leafing value observed in the spatula test is influenced by a variety of factors, among which are the concentration of pigment, its fineness or covering area; the composition of the leafing liquid, its viscosity and drying time; the method of suspending the spatula, whether in a draft or still air or in a cylinder.

3. The investigation of the leafing properties of aluminum pigments is best carried out by making enough measurements to establish the relation between leafing power and pigment concentration and interpreting the data in the light of the covering area of the pigment.

4. The numerical values for leafing power, determined by the spatula test, should include a statement as to the weight of powder taken for the test and the grade of pigment or its covering area.

5. Experimental conditions are suggested for testing the leafing power of vehicles by means of a standard sample of aluminum powder.

Acknowledgment

In the development of the spatula leafing test, various members of the staff of Aluminum Research Laboratories have contributed valuable ideas. The authors wish particularly to acknowledge the assistance of W. E. Giles in this work.

Literature Cited

(1) Edwards, J. D., "Aluminum Bronze Powder and Aluminum Paint", p. 23, New York, Chemical Catalog Co., 1927.
(2) Edwards, J. D., "Aluminum Paint and Powder", p. 31, New York, Reinhold Publishing Corp., 1936.
(3) Edwards, J. D., and R. B. Mason, Ind. Eng. Chem., Anal. Ed., 6, 159 (1934).
(4) Federal Specification, Powder for Paint, No. TT-A-476, Nov. 15, 1932.
(5) Pittsburgh Paint and Varnish Production Club, Natl. Paint, Varnish Lacquer Assoc., Sci. Sect., *Circ.* 546, 297 (Nov., 1937).
(6) Wray, R. I., *Official Digest, Federation Paint & Varnish Production Clubs*, No. 169, 331 (Nov., 1937).

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Saccharification of Starchy Grain Mashes for the Alcoholic Fermentation Industry

USE OF MOLD AMYLASE

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Two strains of the mold *Aspergillus oryzae* have been found very satisfactory for producing amylase for use in saccharifying corn fermentation mashes. Best conditions for the production of highly active amylase preparations by growing the molds on wheat bran in rotating drums have been developed and are described. Data are presented for experimental fermentations in which the moldy bran was used for saccharifying the mashes; the effects of grinding, proportion of moldy bran, and temperature of saccharification were particularly investigated. Best results are obtained when the moldy bran is employed in the same manner as malt. On the average the moldy bran produces approximately 12 per cent higher alcohol yields than does a good dried barley malt. The possibilities of using the moldy bran to replace malt in the alcohol fermentation industry is discussed.

WHEN starchy substrates, such as the various grains or potatoes, are employed for the production of alcohol, the starch must first be converted to sugars before the yeast is introduced. This is usually done by adding malt (most commonly prepared by sprouting barley) which contains considerable quantities of the biological catalyst, or enzyme, of saccharification called "diastase" or "amylase." The authors prefer to use the term "amylase" since it avoids confusion that sometimes results from the fact that "diastase" is the French term for enzyme.

Many microorganisms produce amylase, and processes making use of microbial amylase for various purposes have been introduced into many countries. Certain molds have been found to be especially active in producing amylase. The literature on the use of microbial amylase in the fermentation industry has been reviewed by Smyth and Obold (*8*) and by Thaysen and Galloway (*11*). Amylase produced by molds has been used for centuries in the Orient, particularly in Japan, where *koji*, an amylolytic preparation obtained by growing suitable molds on steamed rice (*9*), is used instead of malt. It has been suggested that mold amylase might well be employed also in the fermentation industries of occidental countries. One development along this line is the Amylo process for the manufacture of alcohol, in which molds of the genera *Mucor* or *Rhizopus* are grown directly in the mash in order to convert the starch before yeasting. The papers of Galle (*4*), based on practical experience with the working of the Amylo process, and of Owen (*6*) most adequately describe the status of this method.

Takamine (*10*) patented the use of molds for the production of amylase preparations; one commercial product is marketed as "Taka-diastase." Use of mold preparations to replace malt in the fermentation industry was suggested by Takamine, and large-scale tests at the plant of Hiram Walker and Sons, Inc., in Canada in 1913 (*9*) proved entirely successful, yields of alcohol being better than with malt. However, a slight off-flavor or odor was produced in the alcohol, and since the flavor is of paramount importance in beverage alcohol, Takamine's preparation has not found favor in the alcohol industry. Now, however, with the increasing interest in power alcohol, it would seem that a procedure similar to Takamine's should hold much promise for production of industrial alcohol. Since the details of a workable process using mold amylase had not hitherto been well established, the purpose of the present investigation was to develop methods for culturing molds in order to produce an active amylolytic preparation, and to study the use of this material in saccharifying grain mashes for alcoholic fermentation.

Preliminary Studies

The saccharifying power of an enzymic material may be determined and expressed in degrees Lintner according to the Official Method of the American Society of Brewing Chemists (*1*) or by the method as modified by Anderson and Sallans (*2*). However, the Lintner numbers obtained for different materials, such as malt, soybean, different mold cultures, etc., have little meaning with regard to the relative merits of these different materials for saccharifying fermentation mashes. The usefulness of an amylolytic material for converting fermentation mashes can be determined accurately only by running fermentation tests. Hence, all results as given in this paper are based upon fermentation experiments.

Preliminary tests were made on amylase production by eight species of bacteria and twenty-one species or strains of molds. None of the bacteria gave very promising results. Of the molds tested, several strains of *Rhizopus* species and three strains belonging to the *Aspergillus flavus-oryzae* group were found to possess the highest amylolytic activity. For cultivation of the molds in flasks, several media were tried, including corn mash, moistened distiller's grains, and moistened wheat bran. The latter medium gave by far the best results and was therefore adopted for further work. Growth of the several *Rhizopus* species was in general less rapid and uniform than that of the *Aspergillus* cultures. Hence attention was concentrated on the Aspergilli. The three cultures selected, with their laboratory numbers, were as follows: culture 2, *Aspergillus oryzae*, secured from the American Type Culture Collection as No. 4814; culture 10, *A. flavus*, secured from Thom as No. 3538; culture 22, *A. oryzae* isolated from oat hulls by the author. The three selected cultures were continuously cultivated on agar slants and on moistened bran. Cultures 2 and 22 were plated to test for purity and no contamination was found. Individual colonies were selected for further cultivation.

The three mold cultures grew well on moistened bran. With cultures 2 and 10, only moderate sporulation occurred in 4 days, and incubation for at least a week was found necessary for abundant sporulation. Culture 22 produced a heavy crop of spores in 4 days. Likewise, the latter culture was observed to cause less lumping during growth. The optimum temperature for cultivation of the three mold cultures was found not to be very definite, but all grew best within the range 25° to 35° C.; the optimum was at about 30° C. Growth was somewhat limited at 38° C., and the cultures failed to grow at 42° C.

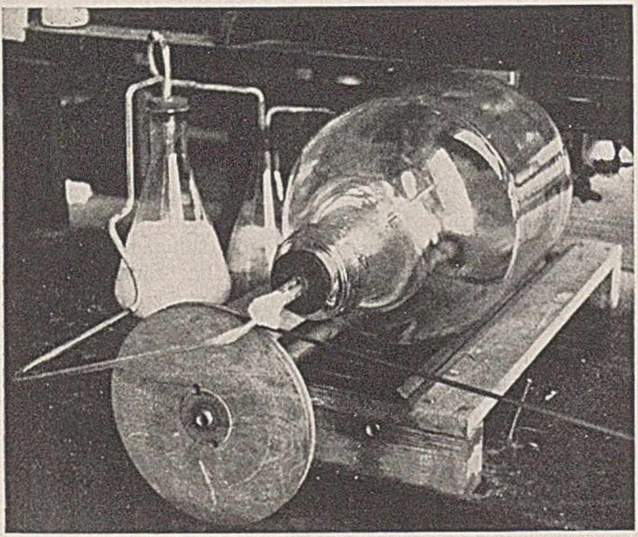

FIGURE 1. LABORATORY APPARATUS FOR GROWING MOLDS IN A ROTATING 5-GALLON PYREX GLASS BOTTLE (AERATION FROM THE COMPRESSED AIR SUPPLY)

Since the growth of many microorganisms which might cause contamination of mold cultures is prevented by an acid reaction of the medium, use of dilute acid instead of water to moisten the bran in preparing the medium was investigated. Mold growth was satisfactory when hydrochloric acid up to 0.3 N was employed. Growth of culture 2 was a little more rapid when water was used, but sporulation was heavier in the acidified mashes. Little difference was observed in the growth or sporulation of culture 22 in either the mash prepared with water or with dilute acid.

Preliminary investigation of the amylolytic activity of the molds selected was made by means of the moldy brans resulting from the growth of the molds on moistened wheat bran in flasks. The moldy brans were used for saccharifying corn mash for fermentation tests; in the several series of fermentations different proportions of the moldy brans and various temperatures were used during the saccharification period. However, the results were exceedingly variable. This was believed to be due to the difference in the growth of the molds in the various flasks from day to day, and to lack of uniformity in the product which resulted from the excessive matting and lumping occurring during the growth. Hence, equipment was developed for cultivating the molds in larger quantities and in a more reproducible manner.

The apparatus developed (Figures 1 and 2) was simply a rotating drum through which a stream of sterile air could be passed for aeration of the growing mold. The drum used was a 5-gallon container (either a Pyrex bottle or an iron can) which was mounted on a system of rollers to serve as a support as well as a rotating device. The current of air could be passed into the drum by means of a glass or iron tube reaching through the stopper nearly to the bottom of the drum. The outlet for the air also passed through the stopper. The air was sterilized by bubbling through sulfuric acid and then humidified by passing it through sterile distilled water. The use of this equipment resulted in rapid mold growth with little matting and lumping; the moldy product was more uniform and possessed greater diastatic activity than that produced in flasks. All the data included in this paper were obtained with mold preparations produced in the rotating drums.

Methods Adopted

As a result of the preliminary studies, the following methods were adopted for the study of mold amylase in saccharifying corn mash for alcoholic fermentation:

The stock mold cultures were grown on slants of sterile solid media in test tubes. Both wort-agar and glycerol-yeast extract-agar media were found suitable. For cultivating the molds in flasks, a bran mash was used. This was prepared by thoroughly mixing wheat bran with about an equal weight of distilled water and sterilizing for an hour at 20 pounds per square inch (1.4 kg. per sq. cm.) steam pressure. For best results it was found that the mash should contain from 50 to 70 per cent of water. About 30 grams of bran were used in a 500-ml. Erlenmeyer flask, or 50 grams in a 1000-ml. flask. Growth and sporulation were seriously retarded when larger quantities of bran were

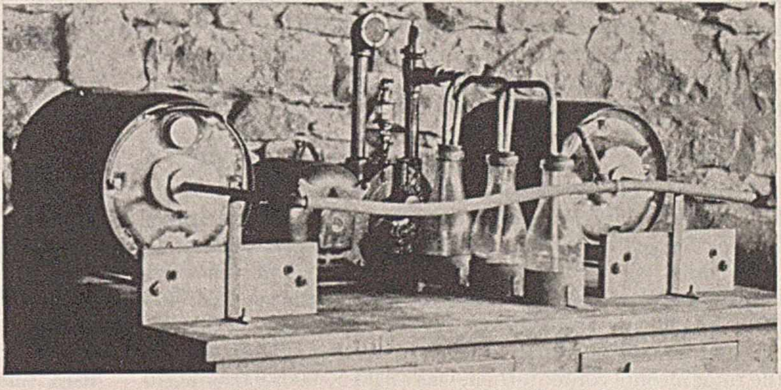

FIGURE 2. LABORATORY EQUIPMENT FOR GROWING MOLDS IN 5-GALLON IRON CANS UNDER FORCED AERATION AND WITH CONTINUOUS ROTATION

used, as a result of insufficient access of air to the mass. Rather heavy inoculations of the bran mash were made from well-sporulated slant cultures of the mold or, more conveniently, from well-sporulated cultures grown on the surface of sterile beer wort. The flasks were shaken every 4 to 8 hours to diminish matting and lumping of the contents as much as possible. Incubation was at 30° C.

Mold Growth in Rotating Drum. The drum is charged with 1000 to 1200 grams of wheat bran well mixed with the requisite amount of water to give a final proportion of 50 to 70 per cent moisture. The drum and mash are sterilized by heating in the autoclave for 2 hours at 20 pounds per square inch steam pressure. After being cooled to room temperature (about 25° C.), the mash is inoculated with 2 to 5 per cent of a well-sporulated bran mash culture of the mold grown in a flask. The contents of the drum are then mixed by rotation. A slow stream of air is passed into the drum, and during the germination period (from 12 to 16 hours under normal temperature conditions) the drum is rotated for not more than 15 to 20 minutes each 2 hours. The active growth of the mold becomes evident by a rise in temperature of the mass. After growth is well started, the rotation may be continuous or intermittent, but the speed of rotation should not surpass 1 r. p. m. Slow continuous rotation is preferable, and increased aeration with cool air saturated with moisture becomes necessary. The aeration is so regulated as to keep the temperature a little below 35° C. During the active growth period the bran assumes a white appearance due to mycelial development; sporulation of the mold changes the color to yellow-green. At the end of 40 to 54 hours the drum is stopped, and the moldy bran is spread out on papers and dried at room temperature. The dried material is then ground in a burr mill to a coarse powder and as such is employed to saccharify corn mashes for fermentation in much the same manner as malt is used.

Fermentation Tests. Into each 1000-ml. Erlenmeyer flask were introduced 100 grams of corn meal, 1 gram of malt or moldy bran, and 500 ml. of water which had been heated to 80° C. The contents were mixed thoroughly by shaking and then allowed to stand for about 30 minutes. This "premalting" period was required to produce preliminary liquefaction of the raw starch and thus prevent the mash from becoming too thick and lumpy on subsequent cooking. After being cooked for 60 minutes at 20 pounds per square inch steam pressure, the mash was cooled to the conversion temperature and kept there by placing the flasks in a constant-temperature water bath. Weighed quantities of the amylolytic material were added, and the temperature was maintained for 60 minutes, the contents of the flasks being agitated frequently. After this period the mash was cooled to incubator temperature (30° C.) and inoculated with an active culture of yeast growing in beer wort or molasses medium, 50 ml. of inoculum being used per flask. After incubation for 3 days, the final volume of the fermented mash in each flask was measured, a 300-ml. aliquot distilled into a 100-ml. volumetric flask, and the alcohol content of the distillate determined by measuring the specific gravity (d^{25}_{25}) with a Chainomatic Westphal balance; the alcohol concentration was read from an appropriate table.

The yellow corn used throughout these experiments was of very poor quality (containing only about 50 per cent starch) as grown in Kansas during the drought year of 1936. The ground corn was analyzed according to the official, direct acid-hydrolysis method of the Association of Official Agricultural Chemists (*3*); the reducing substances formed were estimated by the method of Shaffer and Hartmann (*7*) and calculated as dextrose. The Shaffer-Hartmann reagents were standardized against a sample of pure dextrose.

The experimental results are expressed in the tables as per cent of the theoretical conversion of carbohydrate in the corn to alcohol according to the equation:

$$C_6H_{12}O_6 \longrightarrow 2CO_2 + 2C_2H_5OH \qquad (1)$$

The data given represent the average values for duplicate fermentations, and all yields were corrected for the amount of alcohol derived from the inoculum and amylolytic material. The method of calculation is illustrated by the following example: The final volume of beer in a fermentation flask was 600 ml., and the specific gravity of the distillate from 300 ml. of this beer was 0.9712, representing 18.05 grams of alcohol; the total alcohol content, then, was 18.05 × 600/300 = 36.10 grams. Analysis of control fermentations on the moldy bran employed in preparing the mash and on the beer wort used for growing the inoculum showed that 0.058 gram of alcohol was obtained per gram of moldy bran and 0.029 gram of alcohol per ml. of inoculum. Since 10 grams of moldy bran were used in preparing the mash and 50 ml. of inoculum in the inoculation, alcohol derived from the moldy bran and inoculum in the fermentation was (10 × 0.058) + (50 × 0.029) = 2.03 grams. Hence the alcohol produced from the corn was 36.10 − 2.03 = 34.07 grams. From the theoretical equation, one gram of dextrose should give

$$2C_2H_5OH/C_6H_{12}O_6 = 92/180 = 0.5112 \text{ gram of alcohol}$$

The dextrose equivalent of the corn was 70.0 per cent; then from the 100 grams of corn used in the fermentation, the theoretical yield should have been 100 × 0.70 × 0.5112 = 35.78 grams of alcohol. The actual yield of 34.07 grams therefore represents 100 × 34.07/35.78 = 95.2 per cent of the theoretical yield of alcohol.

Preparation of Moldy Bran

More than fifty batches of moldy bran have been prepared in the rotating drums. The first five runs served to determine the conditions of moisture content, sterilization, inoculation, rotation, and aeration required for the best growth of the molds. It was also determined during this preliminary period that the moldy bran could be air-dried without loss of amylolytic activity and could be stored for extended periods in the dry condition. The conditions found most suitable for preparation of moldy brans of highest amylolytic power are given above in the description of methods used and were adopted for all subsequent runs. For plant-scale use the moldy bran could be prepared in equipment similar to the pneumatic malting drums now in use.

Moldy bran preparations were made from each of the three selected cultures. The most rapid development of the molds began about 12 to 16 hours after inoculation, and mycelial growth was completed in about 40 to 54 hours. Abundant sporulation of culture 22 occurred within this period, but cultures 2 and 10 did not sporulate so heavily. Since the amylase is probably most abundant at the time of sporulation (*5*), it was desirable, when the moldy bran was to be dried, to remove it from the drums and spread it out for drying before extensive sporulation had taken place. It was then observed that during the drying period the sporulation ensued.

Fermentation of Corn Mash Saccharified with Moldy Bran

Several series of fermentations were run in flasks as outlined above for the purpose of testing the amylolytic activity of moldy bran preparations from the various runs and to determine the best method of using moldy bran for saccharification of the fermentation mashes to give maximum alcohol yields. The latter included investigations of the effect of drying the moldy bran and of grinding it, and determination of the optimum temperature for conversion of the mashes by the mold amylase and of the proportion of the moldy bran required to give maximum alcohol yields.

Each of the moldy bran preparations from the several runs was subjected to fermentation tests. The results of some typical fermentations are given in Table I. The mashes were saccharified according to customary malting practice for 60 minutes at 50–55° C. by means of air-dried and ground moldy bran, equivalent to approximately 10 per cent of the weight of corn in the mash. Tests 1 to 4 (Table I) were run at a different time from the others. The results show little difference in alcohol yields when moldy bran of either culture 2 or 22 was used for saccharifying the mashes. Culture 2 was apparently slightly superior. Rather uniform yields were obtained with the various preparations from different runs with the same culture. Culture 10 yielded a preparation definitely inferior for saccharifying a fermentation mash. The better moldy brans gave greater alcohol yields than did malt controls, averaging about 12 per cent higher.

TABLE I. FERMENTATION TESTS WITH MOLDY BRANS

Test No.	Mold Culture No.	Drum Run No.	Alcohol Yield, % of Theory	Test No.	Mold Culture No.	Drum Run No.	Alcohol Yield, % of Theory
1	Malt	Control	80.0	8	2	19	93.9
2	2	5	78.0	9	22	5	92.4
3	2	9	83.5	10	22	16	91.6
4	2	10	87.6	11	22	19	91.3
5	2	11	90.0	12	10	8	68.7
6	2	13	97.4	13	Malt	Control	80.5
7	2	18	92.9				

A fermentation experiment in which varying proportions of both ground and unground moldy bran were employed in saccharifying the mashes showed that grinding the dried material increased the yields slightly at every proportion. For example, when 10 per cent moldy bran of the weight of corn was used, the alcohol yields were 76.4 and 78.8 per cent of theoretical for unground and ground material, respectively. Evidently the grinding process makes the enzyme more available for saccharifying the starch. The proportion of moldy bran required to give maximum alcohol yields was 8 to 10 per cent of the weight of corn used. The data of Table II confirm this proportion.

Table II shows the effect of the temperature of conversion and proportion of moldy bran required to produce maximum alcohol yields. The moldy brans used were dried and ground, and the mashes were saccharified at the indicated temperatures for 60 minutes. The results in *A* indicated that the highest conversion temperature employed (50–55° C.) is advantageous in the use of moldy bran from culture 2. In another experiment the results were reversed, although somewhat erratic; slightly higher alcohol yields were obtained with the conversion temperature of 40–45° C. There was little difference in alcohol yields throughout the range of temperatures used in the experiment with moldy bran from culture 22; a slight advantage appeared for the lowest temperature employed. These somewhat conflicting results lead to the conclusion that any temperature between 45° and 60° C. is suitable for the saccharification of corn mash before fermentation by moldy brans of cultures 2 or 22.

TABLE II. RESULTS OF VARIATION OF PROPORTION OF MOLDY BRAN AND OF SACCHARIFICATION TEMPERATURE ON ALCOHOL YIELDS

Saccharification Temp., ° C.	Moldy Bran, % of Corn (Dry Basis)	Alcohol Yield, % of Theory	Saccharification Temp., ° C.	Moldy Bran, % of Corn (Dry Basis)	Alcohol Yield, % of Theory
A. Culture 2, Run 13					
40–45	4.88	81.2	45–50	9.67	92.0
40–45	7.23	83.5	50–55	4.88	80.2
40–45	9.67	88.1	50–55	7.23	88.4
45–50	4.88	77.5	50–55	9.67	97.4
45–50	7.23	84.8			
B. Culture 22, Run 16					
45	10.56	93.9	50–55	10.56	91.6
60	10.56	91.3	50–55	7.92	92.0
			50–55	5.36	85.5

In order to test the suitability of moldy bran preparations for the conversion of starchy mashes on a larger scale, four culture tank fermentations were carried out at different times on about 85 gallons of mash in each case. The mashes were prepared and the fermentations were run as follows: Approximately 75 gallons of water were heated in the tank to about 80° C. Vigorous agitation was begun and continued throughout the mashing process. To the warm water were added 90 or 100 pounds of ground yellow corn with about 1 pound (1 per cent on the weight of corn) of malt or moldy bran, and the mash was "premalted" by maintaining the temperature at approximately 60° C. or 30 minutes. Water was then added to make the volume 85 gallons, the tank was closed, and the mash was cooked for 60 minutes at 15 pounds per square inch steam pressure. After being cooled to 55° C., the moldy bran was added to the cooked mash, and saccharification was carried out at 50–55° C. for one hour. The mash was then cooled to 30° C. and inoculated with an active yeast culture in molasses medium. Immediately after inoculation a sample of the mash was taken for the determination of total carbohydrate, reducing sugars, and acidity. The mash was agitated and vigorously aerated for 15 minutes in each hour for the first 6 hours after inoculation. Twelve hours after inoculation the mash was sampled and analyzed for alcohol content and acidity. Subsequently, sampling and analysis were repeated each 4 hours until the maximum alcohol concentration had been reached. Residual carbohydrates were then determined in a sample of the fermented mash or "beer."

In the two cases where sufficient of the ground moldy bran was employed for adequate conversion, the alcohol yields from the culture tank fermentations were as good as or better than those usually obtained with malt. Typical data are given for one culture tank fermentation:

Weight of corn used, 100 lb.
Total weight of starch in mash, 50.62 lb. (=56.24 lb. dextrose)
Moldy bran used, 9.9 per cent of corn (dry basis)
Total carbohydrate (as dextrose) in mash, 56.5 lb. (7.96 gram per 100 ml.)
Residual carbohydrate (as dextrose) in beer, 5.66 lb. (0.80 gram per 100 ml.)
Carbohydrate utilized, 90.0 per cent
Alcohol yield, 90.1 per cent of theory (3.66 gram per 100 ml.)
Final acidity, 5.9 ml. of 0.10 *N* per 10 ml. of beer.

Conclusions

Fermentation tests in flasks have shown that moldy bran prepared with either of the two mold strains of *Aspergillus oryzae* (cultures 2 and 22) gives better results than malt in the saccharification of corn mash for fermentation; the alcohol yields are, on the average, about 12 per cent higher with the moldy bran than with malt. Moldy bran of culture 2 was found to produce slightly higher yields of alcohol than that of culture 22. However, the latter culture grows more rapidly with less tendency to lumping, produces spores more abundantly, and shows greater ability to overgrow contaminants, which would all be important factors when industrial use is contemplated. The moldy bran should be ground before being used in saccharifying mashes and may be employed either wet or dried. Air drying does not affect the amylolytic activity, nor does storing in the dry condition. A proportion of moldy bran of 8 to 10 per cent of the weight of corn in the mash seems to be necessary for maximum alcohol production, and saccharification can be carried out satisfactorily within the range 45–60° C.

Culture tank fermentations have shown that under favorable conditions alcohol yields of at least 90 per cent of the theory can be obtained by the large-scale use of moldy bran for saccharification of corn mash. This alcohol yield is rarely reached with malt, and it would seem that the preparation and use of moldy bran to replace malt in the production of industrial alcohol should hold much promise. The economic advantages of such a process are obvious. Not only can better alcohol yields be expected, but the high cost of malt can be largely eliminated. The raw materials for the preparation of mold amylase preparations, wheat bran, or other similar bulky substance, are much cheaper than barley for the production of malt. Likewise, the duration of the process for the preparation is much shorter for moldy bran than for malt. For plant-scale use it should be possible to prepare the moldy bran without difficulty in equipment similar to the pneumatic malting drums now in common use. The product can then be ground wet and used like green malt, or dried and used like cured malt in the saccharification of the starchy mashes. The problems which are always encountered in going from the laboratory to the plant scale are now being investigated with regard to the production of the moldy bran. In the laboratory an investigation of the use of moldy bran for saccharification of starchy substrates other than corn is now in progress.

Acknowledgment

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Literature Cited

(1) Am. Soc. Brewing Chemists, Official Methods, 1936.
(2) Anderson, J. A., and Sallans, H. R., *Can. J. Research*, **15C**, 70 (1937).
(3) Assoc. Official Agr. Chem., Methods of Analysis, 4th ed., 1935.
(4) Galle, E., *Z. angew. Chem.*, 36, 17 (1923).
(5) Oshima, K., and Church, M., Ind. Eng. Chem., 15, 67 (1923).
(6) Owen, W. L., *Ibid.*, 25, 87 (1933).
(7) Shaffer, P. A., and Hartmann, A. F., *J. Biol. Chem.*, **45**, 365 (1921).
(8) Smyth, H. F., and Obold, W. L., "Industrial Microbiology", Chap. 32 (1930).
(9) Takamine, J., J. Ind. Eng. Chem., 6, 824 (1914).
(10) Takamine, J., U. S. Patents 525,819–25 (1894); 525,971 (1894); 562,103 (1896); 826,699 (1906); 975,656 (1910); 991,560–1 (1911); 1,054,324 and 1,054,626 (1913); 1,148,938 (1915); 1,263,817 (1918); 1,391,219 (1920); 1,460,736 (1921).
(11) Thaysen, A. C., and Galloway, L. D., "Microbiology of Starch and Sugars", Chap. II (1930).

Evaluation of Nitrocellulose Lacquer Solvents

Comparison by Means of a Constant Viscosity Procedure

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SEVERAL factors must be taken into consideration when a nitrocellulose solvent is evaluated. These factors vary in their relative importance according to the type of lacquer and the use to which it is applied. When contemplating the adoption of a certain solvent or solvent mixture for lacquer formulation it first becomes necessary to consider such items as the viscosity per unit of solids, hydrocarbon tolerance, cost, evaporation rate, flow-out characteristics, blush, and a number of others. However, the first three—viscosity, hydrocarbon tolerance, and cost—are of almost universal importance, regardless of the type of lacquer or its intended use. The object of this paper is to describe a method for nitrocellulose solvent evaluation by means of which a single value may be assigned to the combined viscosity characteristic and diluent acceptance of the solvent, and which, in turn, may be used to relate this combined solvency value to the cost of application.

Baker (*1*) in 1913 first advanced the use of viscosity of solutions as an indication of the solvent strength of the mixture for nitrocellulose; Sproxton (*7*) in 1920 used the tolerance of the solution for hydrocarbons for the same purpose. These two procedures have been employed extensively in the industry for comparing the ability of solvents to dissolve nitrocellulose, and no satisfactory method has been advanced to replace them up to the present time.

The viscosity and hydrocarbon dilution ratios of a lacquer solvent are commonly classed together under the heading of its "solvency characteristics", but only recently has any material appeared in the literature which attempts to interpret the two sets of data and correlate them into a more flexible and usable form. Doolittle (*2*) approached the problem by the utilization of phase diagrams which provide an evaluation of solvent strength by combining the two. It has been recognized for some time (*5*, *6*) that there are cases where dilution ratio and viscosity actually furnish conflicting indications. Of still greater importance in this connection is the fact that whether they are considered separately or together, they not only fail to supply a satisfactory basis for comparison, but in some cases they tend to exaggerate the differences which exist between two or more solvents or solvent combinations and to minimize them in others. Thus it is both difficult and confusing to attempt to assign a definite solvency value to one solvent as compared with another by considering separately viscosity, on the one hand, and hydrocarbon tolerance, on the other.

That there is a real need for a simple means of correlation of viscosity and dilution values becomes more evident when we consider the drawbacks associated with each of the two methods. The viscosity of a nitrocellulose solution alone in a pure solvent or solvent-coupler mixture does not serve as an adequate indication of solvent strength because costs depend largely upon the extent to which the solution may be diluted with cheaper hydrocarbon. On the other hand, dilution ratios as such are not a dependable criterion of solvency because they furnish information concerning the behavior of a nitrocellulose solution at the point of precipitation only and indicate nothing regarding its properties through all the intermediate stages of dilution until that point is reached. The fact that the end point in hydrocarbon titration is ill defined presents still another disadvantage.

This paper deals with a method, referred to hereafter as the constant viscosity procedure, for simultaneously determining the combined viscosity and dilution effect in such a way that the separate study of the two is eliminated. It affords a direct and simple means of comparing the solvency for nitrocellulose of one material with another at any hydrocarbon dilution over the entire range of spray viscosity under conditions which approach those of actual commercial application. It has the added advantage of not demanding any titration with hydrocarbon; the latter analytical method has been beset with many difficulties, some of which are still not under satisfactory control (*3*). The new method replaces the qualitative "dilution ratio" with a quantitative figure.

The constant viscosity procedure as outlined gives a complete picture of the effect of diluent on the action of a nitrocellulose lacquer solvent and at the same time eliminates the use of dilution ratios.

The data obtained by the constant viscosity procedure may be extended to the calculation of the relative costs of solvents or diluents for actual lacquer application at spray viscosity, and an example of this method of comparison for two solvents with a typical diluent is given in detail.

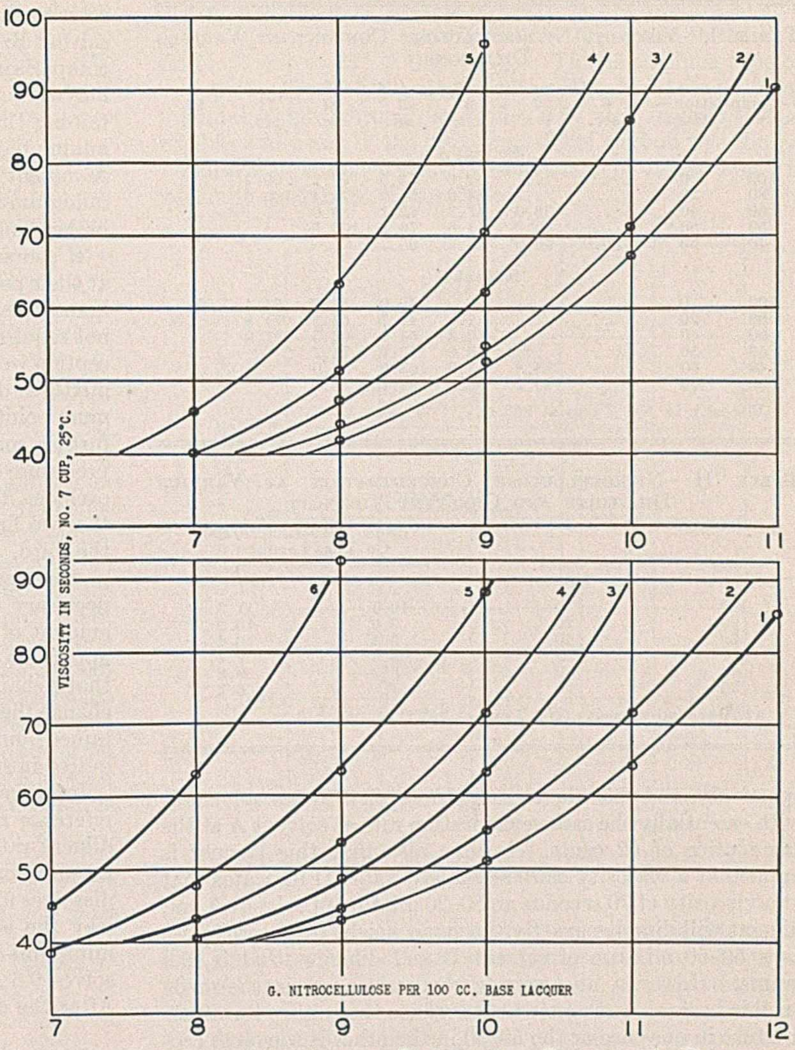

FIGURE 1. VISCOSITY-COMPOSITION CURVES FOR SOLVENT A DILUTIONS (*above*) AND SOLVENT B DILUTIONS (*below*)

1. 100 parts solvent
2. 80 solvent–20 diluent
3. 60 solvent–40 diluent
4. 50 solvent–50 diluent
5. 40 solvent–60 diluent
6. 30 solvent–70 diluent

Constant Viscosity Procedure

Briefly, the constant viscosity procedure for measuring the power of solvent and solvent-diluent mixtures to dissolve nitrocellulose involves viscosity determinations of nitrocellulose solutions in three or more concentrations in the range of spray viscosity. From these data curves are drawn by plotting viscosity against weight of nitrocellulose per 100 cc. of base lacquer. The exact concentration of nitrocellulose at any viscosity within the chosen range may be obtained from the curve. Curves may be set up from experimental data in this way for any number of solvent-diluent mixtures, extending from the pure solvent under test through various degrees of dilution to the point where a cloudy solution is obtained (Table I, Figure 1). The values for nitrocellulose concentration at a standard viscosity as obtained from the curves (Table II) are in themselves an accurate means of comparing the solvency of two or more solvent mixtures; they show the amount of nitrocellulose that will dissolve over a range of dilutions to give a constant viscosity, and thus serve to combine in one set of values all of the information which has previously required both a viscosity determination and a dilution ratio.

The above information is sufficient for ordinary solvent comparison purposes, but its use may be extended further. By plotting the solvent-diluent composition against the concentration of nitrocellulose at any desired viscosity as obtained from the first set of curves, a second curve (Figure 2) is obtained from which the ratio of solvent to diluent which will dissolve a given amount of nitrocellulose at that viscosity may be read. Then, when the apparent values of the diluent and of the solvent in use as standards are known, the comparative value of the solvent strength of any new solvent composition offered to the trade may be established, whether or not its market price is known.

For example, assume that the values of the diluent and solvent A used in a lacquer are 30 and 62 cents per gallon, re-

TABLE I. VISCOSITY-NITROCELLULOSE CONTENT AT VARIOUS DILUTIONS

Composition		Grams Nitrocellulose/100 Cc. Base Lacquer[a]						
Solvent	Diluent	6 sec.	7 sec.	8 sec.	9 sec.	10 sec.	11 sec.	12 sec.
				Solvent A				
100	0	..	..	42.0	52.5	67.2	90.2	..
80	20	..	..	44.0	54.9	71.4	100.3	..
60	40	..	38.0	47.3	62.1	86.0	..	..
50	50	..	40.0	51.6	70.5	100.5	..	..
40	60	36.0	46.0	63.3	96.7	..	..	..
				Solvent B				
100	0	..	..	..	42.9	51.2	64.4	85.5
80	20	..	..	..	44.7	55.1	71.8	..
60	40	..	..	40.3	51.9	63.5	91.0	..
50	50	..	..	43.0	53.7	71.7	..	..
40	60	..	38.8	47.9	63.9	88.0	..	..
30	70	..	45.2	63.2	92.7	..	..	..

[a] Viscosity in No. 7 cup at 25° C.

TABLE II. NITROCELLULOSE CONCENTRATION AT VARIOUS DILUTIONS AND CONSTANT VISCOSITY

Parts Solvent	Parts Diluent	Grams Nitrocellulose/100 Cc. Base Lacquer[a]	
		Solvent A	Solvent B
100	0	10.1	11.3
80	20	9.9	10.9
60	40	9.4	10.4
50	50	8.9	9.9
40	60	8.3	9.2
30	70	..	8.2

[a] At 70-second viscosity (No. 7 cup at 25° C.).

spectively, and that the manufacturer offers a new solvent B with essentially the same evaporation rate as solvent A at the same price of 62 cents. Assume also that this lacquer is applied at a viscosity of 70 seconds. Table II indicates that at a viscosity of 70 seconds an 80–20 mixture of solvent A and diluent will dissolve exactly the same weight of nitrocellulose as a 50–50 mixture of solvent B and diluent—that is, 9.9 grams. However, an accurate comparison cannot be made on this basis since there is no assurance that either the 80–20 mixture in one case or the 50–50 in the other is the most economical under the circumstances. Hence the solvent-diluent mixture of minimum cost for each solvent is established by calculating the relative costs of several different dilutions as obtained from Figure 2 and shown in Table III. These costs are then plotted against nitrocellulose content in each case to obtain cost curves (Figure 3) from which the most economical mixture, or mixture of minimum cost, may be obtained for each solvent.

TABLE III. COST VALUES OF SOLVENT AND DILUENT FOR CONSTANT VISCOSITY AT CERTAIN NITROCELLULOSE CONTENTS AND CORRESPONDING DILUTIONS

Grams Nitrocellulose/100 Cc. Base		Solvent: Diluent Ratio	Cost of Solvent + Diluent[a]	
Solvent A	Solvent B		Solvent A	Solvent B
10.1	11.3	100:0	$0.15399	$0.13676
9.9	10.9	80:20	0.14103	0.12742
9.4	10.4	60:40	0.13177	0.12115
9.2	10.1	55:45	0.13041	0.11700
8.9	9.9	50:50	0.13048	0.11660
8.6	9.6	45:55	0.13054	0.11633
8.3	9.2	40:60	0.13058	0.11725
..	8.2	30:70	.....	0.12300

[a] To dissolve 100 grams of nitrocellulose at 70-second viscosity.

As the proportion of lower priced diluent is increased, the cost of the solvent mixture decreases until such a point is reached where the decrease in nitrocellulose solubility overcomes this factor. Figure 3 shows this point to lie close to a nitrocellulose content of 9.2 grams in the case of solvent A and 9.6 grams for solvent B. Figure 2 shows a corresponding solvent-diluent ratio of 55 to 45 for solvent A and 45 to 55 for solvent B. At this point it is possible to set up three separate comparisons: (1) The point of minimum cost for solvent A may be compared with the solvent B–diluent mixture containing the same weight of nitrocellulose; (2) the point of minimum cost for solvent B may be compared with solvent A–diluent at the same weight of nitrocellulose; or (3) the two minimum points may be compared with each other. The broken lines in Figure 3 indicate these three possibilities.

If course 3 is adopted and the two solvents are compared at their points of lowest cost, a labor cost factor is introduced immediately since the same total volume of the two bases is not required to apply a given weight of solids. The only exception would be the entirely fortuitous case in which the two mixtures dissolved identical quantities of solid at the minimum point. Hence such a comparison may be removed from further consideration in this paper. The constant viscosity procedure recognizes the importance of, and to a large extent excludes, the labor cost variable by offering either or both of the two first-named methods of comparison in preference to the third. In either of these two the ultimate value on which cost comparisons are based is the ratio of solvent to diluent necessary to give a lacquer solution containing a standard amount of solids per 100 cc. of solution at a viscosity most applicable to the problem at hand. It should be pointed out that a change in the cost of any of the volatile ingredients may change the solvent-diluent ratio at which minimum cost is obtained, but no additional experimental details would be required in such a case.

In order to complete the comparison of the two solvents, reference is again made to Figure 2. Here the solvent B–diluent ratio which gives the same solvency performance as the minimum-cost solvent A–diluent ratio of 55 to 45 (e. g., dissolves 9.2 grams of nitrocellulose) is 40 to 60. In the same way the solvent A–diluent ratio which corresponds to the minimum-cost solvent B–diluent ratio of 45 to 55 (e. g., dissolves 9.6 grams of nitrocellulose) is found to be 65 to 35. After the correct ratios of solvent to diluent have been thus

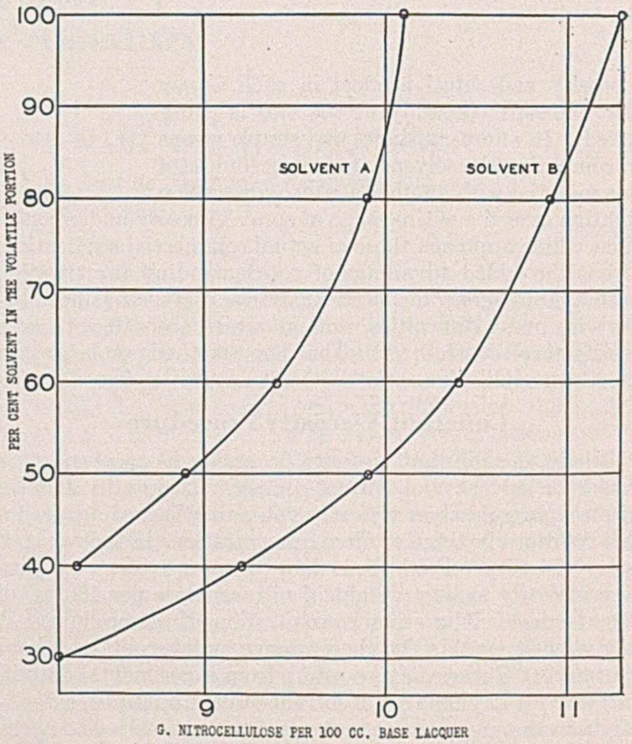

FIGURE 2. SOLVENT-DILUENT NITROCELLULOSE SOLUBILITY CURVES AT 70-SECOND VISCOSITY

established in each case, the true value of solvent B in relation to the standard solvent A at the points of minimum cost for each solvent is merely a matter of calculation (Table IV). At a nitrocellulose content of 9.2 grams, solvent B has an increased value over solvent A in the ratio of 62 to 74 cents per gallon, and at 9.6 grams in the ratio of 62 to 76.2 cents.

As mentioned previously, the comparative value of a new solvent may be established by means of this procedure even though the market price is not definitely known, or the manufacturer may make use of it in setting a tentative value on a new product intended for solvent purposes. In addition, a similar procedure may be followed for the evaluation of a diluent or a solvent coupler simply by comparing its effect on the solvent strength of the solvent to be used with the effect of a diluent of known value on the same solvent.

Conditions of Testing

Since the constant viscosity procedure was devised primarily as a method of comparing the solvent power for nitrocellulose of the numerous solvents now offered for lacquer formulation under conditions approaching those of actual application, an effort was made to simplify the experimental details as much as possible and still maintain high accuracy. For this reason all of the work has been carried out on a volume rather than a weight basis; that is, all nitrocellulose concentrations are in grams per 100 cc. of solution, and all solvent-diluent ratios refer to percentage by volume. This method has the added advantage of being in agreement with the usual plant practice where thinning is done by volume and with actual film application where the important consideration is pounds of solid per gallon of lacquer.

Table IV. Calculation of Value of Solvent B in Terms of Solvent A on a Gallon Basis[a]

	Solvent A	Solvent B
Nitrocellulose/100 cc. base lacquer, grams	9.2	9.6
Solvent A–diluent ratio	55:45	65:35
Value of diluent in mixt. at 30 cents/gal., cents	13.5	10.5
Value of solvent A in mixt. at 62 cents/gal., cents	34.1	40.3
Value of 1 gal. of mixt., cents	47.6	50.8
Solvent B–diluent ratio	40:60	45:55
Value of diluent in mixt. at 30 cents/gal., cents	18.0	16.5
Value of solvent B in mixt., cents	29.6	34.3
Value of 1 gal. of solvent B, cents	74.0	76.2
Comparative value, solvent A to solvent B	62:74	62:76.2

[a] Based on minimum cost points of solvent plus diluent.

A single lot of standard, dry, $^1/_2$-second nitrocellulose was used throughout; since the weights were in the range of 6 to 12 grams, all weighings were made to within ±0.02 gram of the desired amount. For greatest accuracy the weighed nitrocellulose was dissolved in an amount of solvent necessary to make somewhat less than 100 cc. of solution; after the nitrocellulose had dissolved completely, enough additional solvent was added to make the total volume up to exactly 100 cc. All volumes were measured at 25° C. An examination of a number of lacquers made in this manner showed that for the range of concentration employed (6 to 12 grams in 97 to 94 cc. of solvent mixture) the nitrocellulose dissolved to occupy a volume in cubic centimeters of solution equal to half of its numerical weight in grams. This observation was checked closely, found not to affect the accuracy of the results seriously, and adopted. By its use the procedure was simplified considerably in that with a given weight of nitrocellulose the volume of solvent necessary to form 100 cc. of solution could be calculated and added at the beginning (e. g., 10 grams nitrocellulose + 95 cc. solvent mixture = 100 cc. base lacquer).

In this paper the experimental data involve the determination of the quantity of nitrocellulose which solvent-diluent mixtures made up in various proportions will dissolve to give 100 cc. of base lacquer at a viscosity of 70 seconds on the Parlin No. 7 cup at 25° ± 0.1° C. (*4*). This is an efflux type of viscometer in which the time in seconds required for 50 cc. of material to flow through an orifice 0.07 inch in diameter is used as a measure of the viscosity. This method was chosen because of its simplicity and because this type of viscometer is generally used in the lacquer industry.

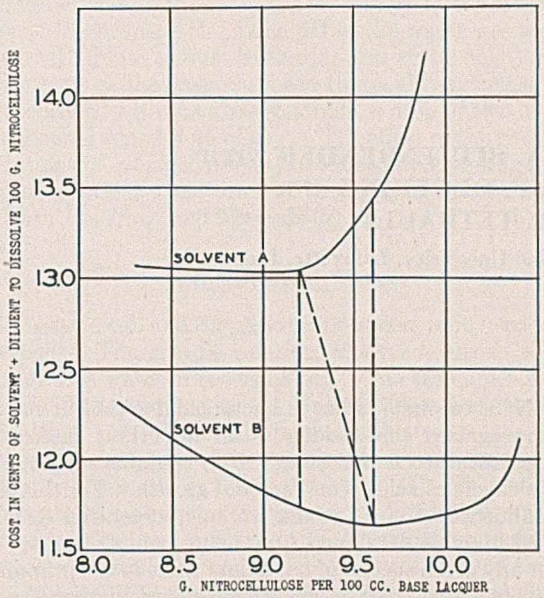

Figure 3. Solvent-Diluent Cost Curves at 70-Second Viscosity

Viscosity values are obtained for three or more nitrocellulose concentrations with each mixture, and the quantity of nitrocellulose is chosen so that at least one value is below and one value above 70 seconds. However, in a later paper which will deal with the constant viscosity procedure as applied to specific solvents diluted with toluene, the viscosity values cover the entire range of practical spraying and demand a larger number of determinations. All samples were tumbled at an identical rate for 24 hours to ensure complete solution. The viscosity measurements were made within 48 hours after the ingredients had been mixed. The recorded viscosity in seconds for the three or more nitrocellulose concentrations with each solvent-diluent mixture is plotted against grams of nitrocellulose, and the curves so obtained are used to express the results as grams of nitrocellulose per 100 cc. of solution at any viscosity common to all the mixtures—in this case, 70 seconds.

By using the above curve and choosing viscosity values at random for purposes of checking the accuracy of the method, it has been established that for nitrocellulose concentrations of 6 to 12 grams per 100 cc. the values obtained are within 0.1 gram of the correct value. Thus in no case can the error be considered to be greater than 2.0 per cent.

Literature Cited

(1) Baker, *J. Chem. Soc.*, 103, 1653–75 (1913).
(2) Doolittle, Ind. Eng. Chem., 30, 199–203 (1938).
(3) Doolittle, *Paint Oil Chem. Rev.*, 99, 26–8 (1937).
(4) Gardner, "Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors", 8th ed., p. 585 (1937).
(5) McBain, *J. Phys. Chem.*, 30, 312–52 (1926).
(6) Mardles, *J. Soc. Chem. Ind.*, 42, 207–11T (1923).
(7) Sproxton, Brit. Assoc. Advancement Sci., *Colloid Rept.*, 3, 82–9 (1920).

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Bactericidal Properties of

Effect of pH

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Phenylmercuric nitrate, Merthiolate, Metaphen, Mercurochrome, tincture of iodine, phenol, Hexylresorcinol, and acriflavine were studied under controlled conditions of pH with respect to their bactericidal properties against *Staphylococcus aureus* and *Escherichia coli*.

Metaphen and Merthiolate could not be adjusted, and acriflavine gave negative results at the concentrations tested. All the others showed increased potency with an increase in the hydrogen-ion concentration of the menstruum. Phenylmercuric nitrate, for example, is effective in a dilution of 1 part in 10,000 at a pH of 7; at a pH of 3 its potency against *Staphylococcus aureus* is increased tenfold. At a pH of 4 phenol showed a 25 per cent increase in effectiveness.

The results indicate that, except for interfering

SINCE the first studies in bactericidal action, it has been recognized that acidity is an important factor. The classical work of Pasteur (1879) contains suggestions as to the effects of acidity on bacterial growth. For this reason the influence of acid media on microorganisms has been studied in much detail and from many points of view.

For any given species of bacterium there is an optimum and relatively narrow pH range which allows vigorous growth. A wider range exists on each side of the optimum over which growth occurs less readily. For most bacteria this optimum pH lies a little to the alkaline side of neutrality (about 7.2–7.6). The wider range of pH over which growth is possible has not been accurately determined for a great many bacterial species. For most pathogenic bacteria, however, it appears to extend between pH values 5.0 and 8.0 (*21*).

On the other hand, it has been shown that chemical compounds are more highly bactericidal in acidic media. The study of the bactericidal power of hydrogen ions began with the work of Paul and Kronig (*18*) in 1896. They studied the action of mercuric chloride in the presence of salts of the noble metals, acids, and bases, and were the first to indicate that bactericidal action in acid media is proportional to the hydrogen-ion concentration or the degree of the electrolytic dissociation. Subsequently, Winslow and Lochridge (*25*) in 1906 substantiated the results obtained by Paul and Kronig (*18*). They calculated the pH of the solutions they studied by means of conductivity data. All of these early workers, however, were handicapped by the lack of a method for the direct determination of hydrogen-ion concentration.

As the methods of adjusting and determining pH were improved and made more readily available, additional work confirmed the previous results. Chick (*4*) in 1910 studied the coagulation of bacteria with hot water and found increasing effectiveness when acidity was produced by an amount of acetic acid too small to be bactericidal in itself. Other investigations made by Norton and Hsu (*17*) in 1916 and Friedenthal (*6*) in 1919 gave similar results. In 1920 Bigelow and Estey (*1*), studying the sterilization of food juices, found that those of low pH were sterilized much more rapidly. These investigators employed electrometric methods for evaluating the pH of the test solutions.

In general, there are two methods of adjustment and determination—the first, by use of buffers and indicators in a comparator, and the second, by direct adjustment with acid or base and electrometric determination (*5*).

There are many examples of each and many types of compounds that have been studied so that only a few instances may be mentioned. Using glycine and citrate buffers, Joachimoglu (*12*) found that mercuric chloride is most effective over a pH range of 5.0 to 6.6 and practically ineffective from 7.8 to 10.1. The same type of buffer solution was also used by Northrop and De Kruif (*16*) in 1922. Using buffered solutions, salicylic, benzoic, and related aromatic acids, and phenols were studied by Vermast (*23*), Waterman and Kuiper (*24*), and Kuroda (*14*). Each found that the free acids are much better than the sodium salts at pH values from 3.4 to 8.4.

In addition, the use of various compounds as urinary antiseptics has provided a further field for investigation of the relationship between pH and antiseptic action. Herrold and Ewert (*10*) studied the antiseptic action of mallophene (β-phenylazo-α,α-diaminopyridine hydrochloride) in urine at various pH values attained by the use of phosphate buffers. Mallophene was also studied by Tetrault (*20*) in an aqueous solution of nutrient agar and glucose. He found minimum effectiveness at a pH of 6.6 and increasing effectiveness at lower pH values.

Mandelic acid, which is rapidly becoming a popular urinary antiseptic, was also found to give better results in acidic media. Rosenheim (*19*) and Holling and Platt (*11*) first used the sodium salt of the acid with ammonium chloride and later the ammonium salt to obtain an acidic urine of pH 5.2 which produced high bacteriostatic action. More recently, Carroll, Lewis, and Kappel (*3*) adjusted the pH of their solutions in urine with a Coleman glass electrode and found that highly acidic media gave good results.

In 1926 Keysser and Ornstein (*13*) postulated that optimum pH is the most important factor in disinfection, stating that "antiseptics are most effective at some definite pH which is different for each group of antiseptics." Thus they found silver nitrate most effective at pH 7.6 and acriflavine most effective at pH 8.0–8.4, but quite ineffective at pH 7.0. Herrold and Ewert (*10*) stated similarly: "It is evident that if the hydrogen-ion concentration influences the optimum range of action of urinary antiseptics, more importance should be given to such observations in urinary infections."

Commercial Antiseptics

factors such as increased insolubility or instability, these diversified antiseptics show a definite increase in effectiveness with an increase in the hydrogen-ion concentration. This is in agreement with the "hydrogen-ion effect" postulated by Goshorn, Degering, and Tetrault (*9*), in their studies of the phenylalkanoic acids. The results do not entirely confirm the statement of Keysser and Ornstein (*13*) that "antiseptics are most effective at some definite pH which is different for each group of antiseptics." They indicate, instead, that the "hydrogen-ion effect" increases progressively up to a maximum for benzoic acid, the phenyl alkanoic acids, phenyl mercuric nitrate, Merthiolate, tincture of iodine, Hexylresorcinol, phenol, closely related compounds, and some inorganic salts.

Recent results of Goshorn, Degering, and Tetrault (*9*) on the bacteriostatic and bactericidal action of benzoic acid corroborated these findings and led them to postulate a "hydrogen-ion effect" which holds for the bacteriostatic and bactericidal action of benzoic acid, related compounds, and salt solutions. It was with the hope of adding further verification to this hypothesis that the present work of studying commercially available antiseptics at controlled hydrogen-ion concentrations was undertaken.

Solutions of Definite pH

The pH of the solutions was measured by the use of a membrane type glass electrode (*2*) with a saturated calomel electrode. They were connected to a Universal potentiometer assembly constructed according to the design of Goodhue (*7*); it contained modifications by H. W. Swank and R. H. Goshorn of Purdue University. The glass electrode was checked against buffer solutions of known hydrogen-ion concentration, before and after each period of use.

The following commercial products were tested as dispensed and at pH values of 3.0, 4.0, 5.0, 6.0, and 7.0:

Phenyl mercuric nitrate,[a] 0.067%
Merthiolate,[b] 1–1000
Metaphen,[b] 1–500
Mercurochrome,[b] 2%
Tincture of iodine[b] (7% iodine, 5% potassium iodide, 82.5% alcohol)
Phenol, 5%
Hexylresorcinol,[b] 1–1000
Acriflavine[b] (neutral), 1–1000
Elixir of mandelic acid[b] (27.2% ammonium mandelate)

An 80 ml. portion of each of the test solutions was placed in a Berzelius beaker into which the electrodes were inserted. The pH of the solution was adjusted by adding 0.1 *N* sodium hydroxide or 0.1 *N* acetic acid dropwise[c]; adequate mixing was ensured by the use of a mechanical stirrer. When the final adjustment of the pH had been made, the solution was transferred to a 100-ml. volumetric flask; the beaker, electrodes, and stirrer were rinsed well with water of the same pH as that of the solution, and the rinsings were added to the volumetric flask. The flask was then filled to the mark with water of the proper pH. (The pH of the water was also adjusted with dilute sodium hydroxide and acetic acid.) After the contents of the flask had been thoroughly mixed, the pH was rechecked with the glass electrode, a drop or two of alkali or acid being added if necessary. The effect of the small concentrations of extraneous ions introduced in adjusting the pH of these solutions was shown to be negligible by the work of Goshorn, Degering, and Tetrault (*9*).

Bactericidal Tests

Escherichia coli and *Staphylococcus aureus* were used as test organisms. The sample solution was made up to a given dilution with water of the same pH. The technique was essentially that described by the United States Department of Agriculture (*22*). The culture was adjusted to the pH of each test before use. The dilution indicated in the table killed in 10 but not in 5 minutes at 37° C. In testing the mercurials, the "retransfer culture" modification was used as described in the Department of Agriculture circular (*22*). Controls of inoculated nutrient broth were run for each pH value tested. The results of these tests on standard pharmaceutical preparations are shown in Table I.

Table I. Results of Bactericidal Tests

pH	Highest Killing Dilution		Lowest Dilution, Positive Growth	
	Staph. aureus	*Esch. coli*	*Staph. aureus*	*Esch. coli*
Phenyl Mercuric Nitrate				
3.0	100,000	400,000	600,000	[a]
4.0	10,000	40,000	20,000	50,000
5.0	10,000	30,000	20,000	40,000
6.0	20,000	10,000	30,000	20,000
7.0	10,000	30,000	20,000	40,000
Merthiolate				
3.0	75,000	100,000	100,000	[a]
4.0	75,000	25,000	100,000	50,000
5.0	10,000	10,000	25,000	25,000
6.0	5,000	5,000	10,000	10,000
7.0	10,000	5,000	25,000	10,000
10.0	10,000	5,000	25,000	10,000
Metaphen				
10.0	1,000	10,000	10,000	25,000
Mercurochrome				
10.0	100	300	300	600
Tincture of Iodine				
3.0	4,000	4,000	[a]	[a]
4.0	3,000	4,000	4,000	5,000
5.0	2,000	3,000	3,000	4,000
6.0	1,500	2,000	2,000	3,000
7.0	1,000	1,500	1,500	2,000
Phenol (*15*)				
3.0	90	100	[a]	[a]
4.0	75	100	90	125
5.0	70	100	75	125
6.0	65	90	75	100
7.0	60	75	65	90
Hexylresorcinol				
3.0	100,000	100,000	[a]	[a]
4.0	12,500	12,500	25,000	25,000
5.0	5,000	5,000	12,500	12,500
6.0	3,000	5,000	5,000	12,500
7.0	3,000	5,000	5,000	12,500

[a] Controls in water at pH 3 did not grow.

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[a] Supplied by The Hamilton Laboratories, Hamilton, Ohio.

[b] Prepared by the School of Pharmacy, Purdue University.

[c] In adjusting solutions of the lower pH values, concentrated acetic acid was used.

Consideration of the data reveals a marked increase in bactericidal effectiveness with an increase in the hydrogen-ion concentration of the menstruum. These results are in agreement with the data obtained from a similar study of the phenyl alkanoic acids (*8*). The marked difference in the structure of these compounds seems to indicate that the "hydrogen-ion effect" (*9*) may be somewhat independent of structure, provided instability or insolubility in acid media are not interfering factors.

Metaphen and Mercurochrome could not be adjusted to the desired pH, hence their solutions could not be checked with respect to the "hydrogen-ion" effect (*9*). Acriflavine gave negative results in the concentrations tested.

Acknowledgment

The authors wish to thank H. Hunt for conditioning of the pH apparatus, and R. N. Shreve of the Chemical Engineering Department of Purdue and V. H. Wallingford of the Mallinckrodt Chemical Works for their interest and support of this project.

Literature Cited

(1) Bigelow, W. D., and Estey, J. R., *J. Infectious Diseases*, **27**, 602 (1920).
(2) Britton, H. T. S., "Hydrogen Ions, Their Determination and Importance in Pure and Industrial Chemistry", New York, D. Van Nostrand Co., 1932.
(3) Carroll, G., Lewis, B., and Kappel, L., *J. Urol.*, **39**, 710 (1938).
(4) Chick, H., *J. Hyg.*, **10**, 237 (1910).
(5) Clark, W. M., and Lubs, H. A., *J. Bact.*, **2**, 1, 109, 191 (1917).
(6) Friedenthal, H., *Biochem. Z.*, **94**, 47 (1919).
(7) Goodhue, L. D., *Iowa State Coll. J. Sci.*, **10**, 7 (1935).
(8) Goshorn, R. H., and Degering, E. F., paper presented before Div. of Medicinal Chemistry at 94th Meeting of A. C. S., Rochester, N. Y., Sept. 6–10, 1937.
(9) Goshorn, R. H., Degering, E. F., and Tetrault, P. A., Ind. Eng. Chem., **30**, 646 (1938).
(10) Herrold, R. D., and Ewert, E. E., *J. Lab. Clin. Med.*, **17**, 49 (1931).
(11) Holling, H. E., and Platt, R., *Lancet*, **1936**, 769.
(12) Joachimoglu, G., *Biochem. Z.*, **134**, 489 (1923).
(13) Keysser and Ornstein, *Klin. Wochschr.*, **5**, 404 (1926).
(14) Kuroda, T., *Biochem. Z.*, **169**, 281 (1926).
(15) Lundy, H. W., *J. Bact.*, **35**, 633 (1938).
(16) Northrop, J. H., and De Kruif, P. H., *J. Gen. Physiol.*, **5**, 127 (1922).
(17) Norton, J. F., and Hsu, P. H., *J. Infectious Diseases*, **18**, 180 (1916).
(18) Paul, T., and Kronig, B., *Z. physik. Chem.*, **21**, 414 (1896).
(19) Rosenheim, M. L., *Lancet*, **1935**, 1032.
(20) Tetrault, P. A., *Med. J. Record*, Sept. 6, 1933.
(21) Topley, W. W. C., and Wilson, G. S., "Principles of Bacteriology and Immunity", Baltimore, Wm. Wood and Co., 1936.
(22) U. S. Food and Drug Administration, *Dept. Agr. Circ.* **198** (1931).
(23) Vermast, P. G. F., *Biochem. Z.*, **125**, 107 (1921).
(24) Waterman, H. I., and Kuiper, P., *Rec. trav. chim.*, **43**, 232 (1924).
(25) Winslow, C. E. A., and Lochridge, E. E., *J. Infectious Diseases*, **3**, 547 (1906).

PRESENTED at the 96th Meeting of the American Chemical Society, Milwaukee, Wis.

SUGAR MANUFACTURE

By Giovanni Stradano
(1536–1605)

The second chemical plate in the "Nova Reperta" shown here, represents the manufacture of sugar as carried out in Sicily about the year 1570. Like the first plate shown in February, it is an engraving by the Brothers Galle of Antwerp from an original painting by Stradano.

This is No. 102 in the Berolzheimer Series of Alchemical and Historical Reproductions.

Again we are indebted to Professor E. C. Watson of the California Institute of Technology, who is the proud possessor of this very rare set of plates known as the "Nova Reperta" (New Discoveries), for his courtesy in supplying a photograph of this engraving.

It is interesting to note the proximity of the factory to the field in which the sugar cane is growing.

D. D. Berolzheimer

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A complete list of the first 96 reproductions appeared in our January, 1939, issue, page 124.
An additional reproduction appears each month.

SETTING OF PORTLAND CEMENT

Thermal Characteristics during Setting at Elevated Temperatures

F. W. JESSEN AND C. E. WEBBER
Humble Oil and Refining Company, Houston, Texas

A method has been developed for a study of the thermal effects in the setting of cement under conditions similar to those encountered in the cementing of oil well casing. A 40 per cent slurry of a standard brand of portland cement was used throughout the investigation. High formation temperatures lead to a rapid setting time of ordinary portland cement. This increased rate of setting is due to the high formation temperature to which the cement is subjected and also to the resulting higher temperature due to the rapid heat evolution during setting. The latter effect contributes quite an appreciable quantity of heat at elevated formation temperatures.

The heat of hydration of a 40 per cent cement slurry has been measured up to temperatures of 150° F. As evidenced by the heat of hydration and the initial setting time, it seems that definite compound formation takes place up to the time of the initial set of the cement. No great temperature effect was noticed during the final set of the cement.

The results of this investigation may well account for the temperature difference found between cement and formations after 12 to 36 hours. Results of this investigation show that at formation temperatures above 120° F. the rapid setting and accompanying heat evolution of the cement make it probable that the cement slurry begins to set well before it is pumped into the desired position. Such a condition would undoubtedly account for many faulty cement jobs.

THE ever-increasing trend toward deeper oil production levels necessitates the placing of cement at temperatures considerably higher than any heretofore encountered. At elevated formation temperatures numerous complications arise in cementing casing, due to the extreme rapidity with which the cement slurry attains its initial set. The purpose of the present investigation was (*a*) to evolve a method for the study of the thermal effects accompanying the setting of cement slurries at temperatures comparable to those encountered in oil well cementing, (*b*) to determine the maximum temperature to which a 40 per cent portland cement slurry might rise when placed in formations of relatively high temperature, and (*c*) to measure the rate of heat evolution from such a slurry at temperatures up to 150° F. Thermal data on the rate of heat evolution was anticipated up to a temperature of 200° F.; however, it became unduly difficult to mix the cement and water to a uniform slurry at 175° F. because of the rapid setting of the cement. Hence, no measurements have been made at temperatures above 150° F. The introduction of special high-temperature cements for oil well cementing has decreased the tendency of rapid initial setting, and it should be possible in the future to determine the rate of heat evolution from these cements at temperatures up to 200° F. The present practice of this laboratory is to determine the thermal properties of cement slurry as well as the physical character of such slurry as an additional guide in selecting oil well cement. When completed, this study of the thermal properties will be the basis for further results to be presented on "special oil well" cements already developed and others now in process of development.

Previous Investigations

Numerous investigators (*1, 3, 5, 8, 11, 12, 15*) have studied the effect of temperature on the setting time of cement and the tensile and compressive strengths. Hemeon (*7*) studied the phenomena of the volume decrease (contraction) and heat evolution accompanying the setting of cement at room temperature. A Carlson vane-type calorimeter (*2*) was used in the experiments to determine the rate of heat evolution; the results thus obtained compared favorably with the customary Dewar flask technique. The heat-of-solution method for evaluating the heat of hydration was employed by Lerch (*10*) and others (*16*). In studying the generation of heat in the hardening of cement used in cementing bore holes, Grozdorskaya and Yaichnikova (*6*) determined that equilibrium between the heat released by the cement and the heat transferred to the surrounding medium is established in 1 to 3 hours. Most of the previous work reported shows that the rate of heat evolution on mixing cement with water attains a maximum value after a time (generally 8 to 15 hours) characteristic of the given cement (*14*). There appears to be no simple relation between the composition of the cement or degree of fineness and the maximum rate of heat evolution (*7*).

Method of the Investigation

Oil well conditions were simulated in that thick masses of cement were avoided, the thickness of the cement wall being from 5 to 8 cm. (2 to 3 inches). This thickness corresponds to the annular space generally employed in oil well cementing practice. A standard brand of portland cement was used in all tests. This cement had the following chemical analysis and physical characteristics:

Chemical Analysis	
Silica	20.60%
Iron and aluminum oxides	9.86
Calcium oxide	66.86
Magnesium oxide	1.27
Sulfur trioxide	1.38
Water	0.03
Loss on ignition	0.07
Total	100.07

Mesh Fineness	
On 100	2.5%
Passed 100 on 200	12.0
Passed 200 on 325	71.0
Passed 325	14.5
Total	100.0
Normal consistency	24%

The cement met all requirements of the A. S. T. M. specifications for portland cement.

The apparatus (Figure 1*A*) used for determining the maximum temperature to which the cement might rise was extremely simple:

A 2-gallon, well-insulated stone jar served as a thermostatic bath. It was equipped with an electric heater, a stirrer, and a sensitive thermoregulator for controlling the temperature of the water bath. In the bath was placed a tin container, 10 cm. in diameter and 15 cm. deep, which served as a mold for the cement. The water bath surrounding the mold was maintained at a constant temperature, the greatest variation being ±0.2° F. or approximately 0.1° C. All temperature measurements were read on a calibrated thermometer with an accuracy of ±0.1° F.

One thousand grams of cement and four hundred grams of water were mixed thoroughly in the mold at room temperature, giving a mass which filled the mold to a depth of 9 cm. Immediately upon being mixed, the mold was placed in the water bath. A 6-mm. glass test tube which extended into the cement to a depth of 5 cm. (2 inches) served as a thermometer well. Water was used as the thermometer well fluid. The temperature of the cement was recorded at regular intervals until the final set had been reached. Six separate experiments were made, one at each of the following temperatures: 80°, 100°, 120°, 140°, 160°, and 180° F. No correction due to evaporation of water from the cement slurry was made, since any loss of water by evaporation could have taken place only while the cement was at a greater temperature than that of the surrounding bath. By the time this occurred, the cement had in every case practically reached its initial set. The results of this investigation at the various temperatures are presented by Figures 2, 3, and 4.

In order to study the actual increase in the rate of heat evolution with temperature, the following method was employed:

A 40 per cent portland cement slurry was used in all instances, the amount of cement used being 150 grams. Figure 1*B* illustrates the apparatus. The calorimeter consisted of a 500-cc. Dewar flask. A 250-cc. volume of water was placed in the flask to provide an adequate water bath. The calorimeter was equipped with a copper coil, through which cooling water could be circulated, a heating element, and a motor-driven variable-speed stirrer to maintain proper thermal conditions. A copper container was used; it was 4.5 cm. (1.75 inches) in diameter and 8.25 cm. (3.25 inches) high, and was made of thin sheet copper which allowed maximum conductivity from the inside of the setting cement mass to the bath. This container fit snugly inside the cooling coil so that any heat emanating from the cement mass was immediately dissipated to the bath. Cooling water flowed through the copper coil, the rate being regulated by means of a pinch clamp. The inlet and outlet temperatures of the circulating water were measured to within 0.05° F. with accurately calibrated thermometers. The inlet water was maintained approximately 10° F. below that of the calorimeter by means of an auxiliary heated and thermostatically controlled bath. Heat losses were minimized by placing the Dewar flask in a water bath which was kept at the same temperature as the calorimeter. Under these conditions this type of calorimeter was considered to give results as accurate as those obtainable with the Carlson vane-type calorimeter (*2*).

In later experiments to test the reliability of the data at 125° F., the cooling coil was eliminated from the calorimeter, and water was allowed to flow directly into the Dewar flask. The Dewar flask was closed with a tight-fitting rubber stopper, the center of which was cut so that the copper container for the cement could be slipped into place through the center hole. After the cement had been lowered into the water in the calorimeter, the center hole was stoppered tightly. Since the cement slurry in the mold was completely covered with water through the test period, no water evaporated from the cement. A mercury seal was provided on the stirrer to prevent water from entering the Dewar flask. The whole calorimeter was then submerged in the outer bath. A sketch of the setup is shown in Figure 1*C*. This procedure also necessitated a change in the method of maintaining the cooling water at a constant temperature. A large copper coil was immersed in the outer bath in which the calorimeter was placed, to assure the inlet water a temperature within a few tenths of a degree of the calorimeter temperature. The inlet and outlet water temperatures were measured in the same way as before. Such a small temperature difference between the inlet water and the calorimeter meant that a greater volume of fluid had to be passed through the calorimeter. The results of this test checked the data obtained in the first series of tests and are given in Figure 5.

The desirability of having the cement, mixing water, and calorimeter as nearly as possible at a uniform temperature is obvious; hence, prior to making any determinations of the rate of heat of hydration, they were brought to the same temperature. The cement slurry (150 grams of cement and 60 grams of water) was mixed by means of a small spatula in the copper mold, and the container was immediately submerged in the water of the calorimeter. This procedure eliminated any transfer of the cement slurry and therefore reduced heat losses before placement in the calorimeter. The greatest variation in temperature between the cement paste after mixing and the water of the calorimeter was 2° F.

The adiabatic heat evolution of the cement was observed by means of the calorimeter that was used in the previous tests, and a heating coil was inserted in the water bath surrounding the

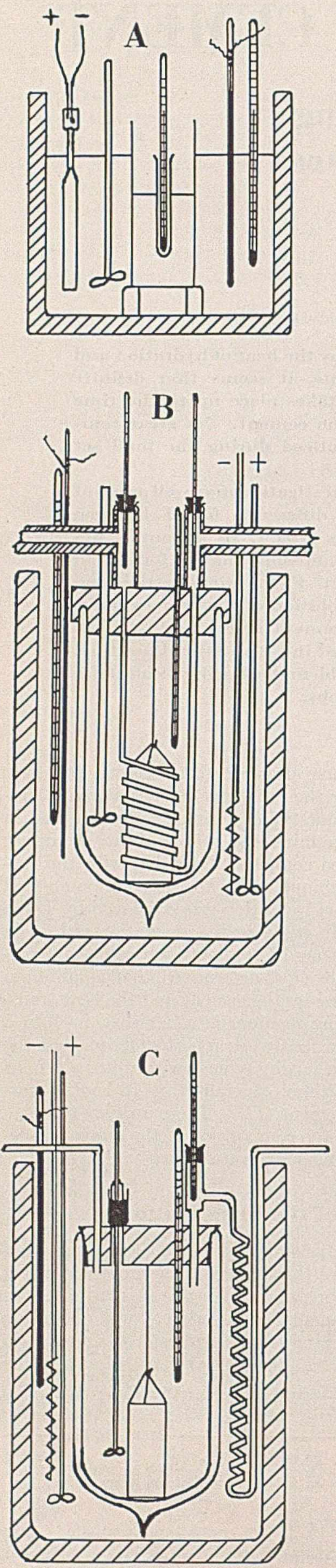

FIGURE 1

A. APPARATUS FOR DETERMINING MAXIMUM TEMPERATURE TO WHICH THE CEMENT MIGHT RISE

B. APPARATUS FOR STUDYING INCREASE IN RATE OF HEAT EVOLUTION WITH TEMPERATURE

C. ARRANGEMENT OF CALORIMETER TO TEST RELIABILITY OF 125° F. DATA

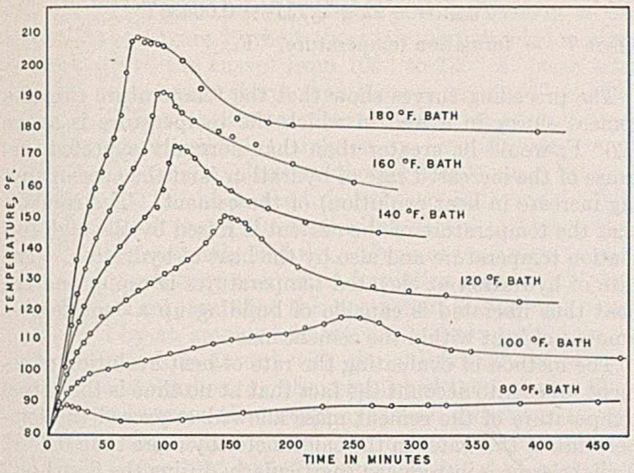

FIGURE 2. TEMPERATURE CHANGES IN CEMENT ALLOWED TO SET AT VARIOUS BATH TEMPERATURES

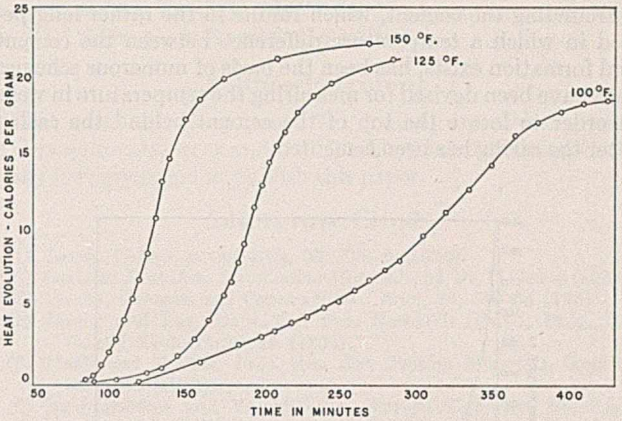

FIGURE 5. HEAT EVOLUTION OF CEMENT AT ELEVATED TEMPERATURES

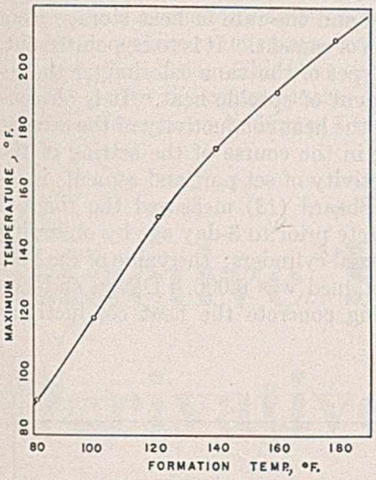

FIGURE 3. TEMPERATURE ATTAINED BY CEMENT AT VARIOUS FORMATION TEMPERATURES

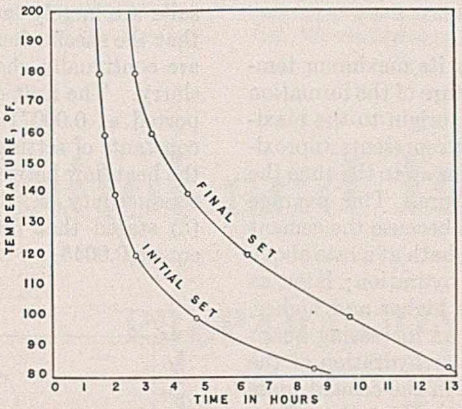

FIGURE 4. EFFECT OF TEMPERATURE ON INITIAL AND FINAL SET OF CEMENT

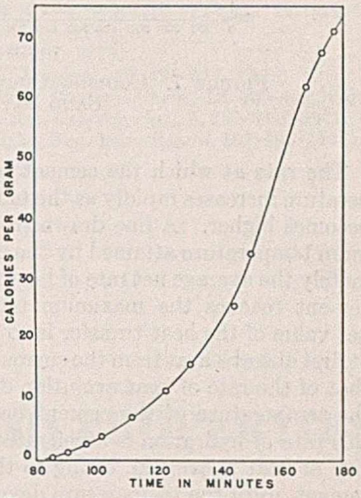

FIGURE 6. HEAT EVOLUTION OF CEMENT UNDER ADIABATIC CONDITIONS

cement mass. A voltmeter and an ammeter were placed in the line to measure the amount of energy required to maintain the water in the calorimeter at the same temperature as that of the cement. In this particular test the temperature of the cement and the water at the beginning were both 110° F. The duration of current flow through the heating coil was measured with a stop watch. At times the current flow was intermittent. Two hundred grams of cement and eighty grams of water were used to form the slurry in this instance. Three hundred cubic centimeters of water were used in the calorimeter. The temperature of the calorimeter rose slowly at first, and then increased rapidly until at the end of 180 minutes the temperature was 210° F. The test was discontinued at this point, the cement having reached an initial set far earlier in the course of the determination. The result of this experiment to determine the heat evolution of cement under adiabatic conditions is shown in Figure 6.

Figure 4 illustrates the time required for the initial and the final sets determined with the Gilmore needle. The time of the initial set in each case just follows the time required to reach the maximum temperature.

Discussion of Results

As Figure 2 shows, the temperature of the cement rises fairly uniformly until it reaches the temperature of the bath. A rapid increase in temperature then occurs with the result that the temperature of the cement passes through a maximum and then drops gradually to the temperature of the bath, remaining there for the time required to attain the final set. As the temperature of the bath is raised, the rate of rise of the cement temperature increases, and in each case a maximum is reached which is above that of the bath; this maximum is 30° F. when the formation temperature is 180° F. No appreciable increase in temperature was noticed while the cement reached its final set. The rather rapid decrease in the temperature from that of the maximum, indicated by the curves in Figure 2, does not actually occur in practice. It is considered that the maximum temperature reached, as indicated by these experiments, is approximately the true value; however, it is readily understood that the decrease of the temperature from the maximum value to that of the formation is not as rapid as Figure 2 indicates. That this decrease in temperature is much slower is shown by Figure 7, which plots the temperature decrease with time of a mass of cement comparable to that used in previous tests when placed in a well-insulated sand bath rather than the water bath. At the end of 18 hours there was still a difference in temperature of 3° F.; after 27 hours this difference had reached 1° F. The low heat conductivity of the cement and the formations generally surrounding the cement, which results in the rather long period in which a temperature difference between the cement and formation exists, has been the basis of numerous schemes that have been devised for measuring the temperature in wells in order to locate the top of the cement behind the casing after the casing has been cemented.

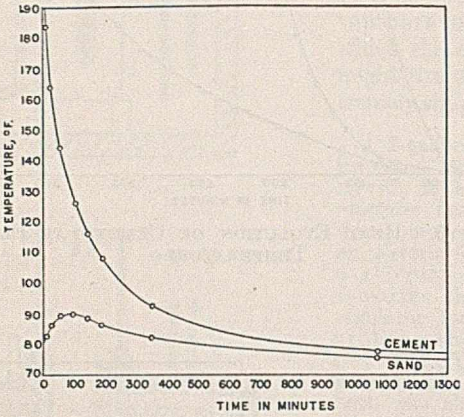

Figure 7. Cooling Curve of Cement in Sand Bath

The rate at which the cement reaches its maximum temperature increases rapidly as the temperature of the formation becomes higher. A line drawn from the origin to the maximum temperature attained by the cement represents approximately the average net rate of heat transfer up to the time the cement reaches the maximum temperature. This average net value of the heat transfer is so called because the cement at first absorbs heat from the surrounding bath at a rate above that of the rate of heat evolution due to hydration; later, as the temperature of the cement becomes higher and higher, this rate of hydration is accelerated and an increasing quantity of heat is evolved, owing to the faster hydration of the cement, until the temperature developed in the cement mass is greater than that of the surroundings. Heat then flows from the cement to the bath.

The temperature developed in the cement at a bath temperature of 80° F. except for the rather rapid rise in the first 15 minutes (which may be attributed to the initial wetting or hydration of the cement) is quite moderate. The rate of this temperature rise is also very low. It thus appears that with a temperature somewhat lower than 80° F., the average net heat transfer rate mentioned above would be zero, and no maximum value of temperature would be reached. That is, the rate at which heat is evolved in the cement would be equal to the rate at which heat is dissipated from the cement, with the result that the temperature-time curve would be a straight line. This is very nearly the case at 80° F. However, when the cement is allowed to set at an elevated temperature, the time required for the same amount of hydration is less, which results in heat being stored up within the cement mass and the consequent rapid rise in temperature above that of the bath.

The data obtained allows a calculation of the maximum temperature to which the cement will rise when placed in a formation having a known temperature. Such a calculation presupposes conditions generally attained in oil well cementing practice and is, of course, not applicable to large masses of cement more common to general construction work. Figure 3 was constructed by plotting the maximum temperature attained in the cement at the formation temperature against the temperature of the formation. The equation of this curve is given by:

$$T_{\text{max.}} = -92 + 2.72T - 0.00586T^2$$

where T = formation temperature, ° F.

The preceding curves show that the temperature rise of a cement slurry in a well in which the temperature is above 120° F. would be greater than that normally expected, because of the increased rate of hydration (and the accompanying increase in heat evolution) of the cement. The result is that the temperature of the cement is raised by the high formation temperature and also by the heat of hydration. The rate of hydration at elevated temperatures is rapid, and the heat thus liberated is capable of building up a considerable amount of heat within the cement mass.

The method of evaluating the rate of heat evolution of cement takes into account the fact that at no time is the actual temperature of the cement mass allowed to exceed the temperature of the water in the calorimeter by more than 0.2° F. A slight error is introduced (particularly during the first 1 or 2 hours of setting at elevated temperature) when the heat evolution from a cement slurry is measured by means of a calorimeter such as the Carlson vane type (*2*) which assumes a constant specific heat for the cement mass and calculates the heat stored in the sample and the rate of heat storage from the heat capacity per gram of cement. It is to be pointed out, however, that in recent types of the vane calorimeter the results are largely independent of specific heat. It is obvious that the specific heat and the heat conductivity of the cement are continually changing in the course of the setting of the slurry. The heat conductivity of set portland cement is reported at 0.00071 (*9*). Sheard (*13*) measured the thermal constants of setting concrete prior to 3-day age by observing the heat flow between coaxial cylinders; the value of the heat conductivity, K, thus obtained was 0.006. Davey and Fox (*4*) stated that for setting concrete the heat conductivity equals 0.0045.

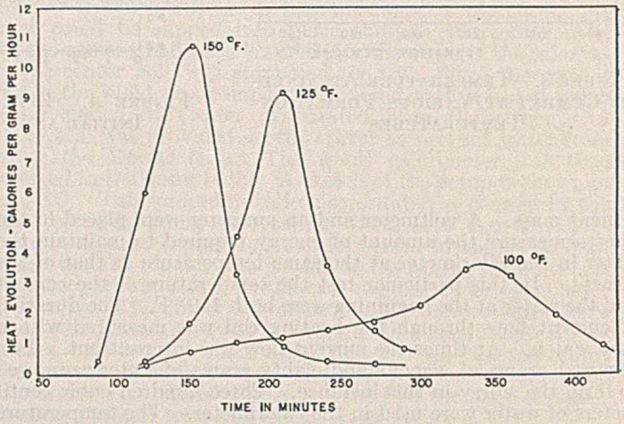

Figure 8. Rate of Heat Evolution of Cement

Figure 5 shows the heat evolution in calories per gram of cement at 100°, 125°, and 150° F. The total heat evolution up to the time of the final set is much the same in each case; however, since the setting of cement varies with the temperature, and because the setting is accompanied by a certain evolution of heat, quite a difference exists in the actual amount of heat liberated at various time intervals. Thus an equal amount of heat is liberated in 2 hours at 150° F. and 4.5 hours at 100° F., and it is easily recognized why the cement set is accelerated at elevated temperature.

Figure 8 shows that the rate of heat of hydration increases rapidly between 100° and 125° F. Between 125° and 150° F. the rate of increase is not as great as that between 100° and

125° F. This characteristic of this portland cement is also noticeable on Figure 2, where there is a more decided increase in the slope of the curves from 100° to 120° F. (each after reaching bath temperature) than there is from 120° to 140°. Since the slope of the curves after they reach the temperature of the bath is dependent mainly on the heat of hydration, it seems that there is a somewhat greater rate increase between 100° and 120° F. than there is between 120° and 140° F. Likewise the slopes of the succeeding curves at higher temperatures increase only slightly. These observations tend to indicate that definite compound formation was taking place at the initial set, and that this compound formation was accompanied by an amount of heat which characterizes the reaction. This is in accord with the observations of Woods, Steinour, and Starke (*16*) who established the fact that there is a relation between the heat of hydration and chemical composition of the cement. Also, the rate of this reaction, as evidenced by the heat evolution, is rather constant, and is not influenced appreciably by temperatures between 125° and 150° F.

On Figure 6 is plotted the heat evolution from cement when allowed to set under adiabatic conditions. It is immediately discernible that the total amount of heat evolved under these conditions is three to four times that evolved at 150° F. in the same length of time. This behavior would be expected, since no heat leaves the cement mass. This fact, in conjunction with the data given in Figure 7, well accounts for the low heat flow from cements which set at temperatures of 150° to 200° F.—i. e., under oil well conditions.

Acknowledgment

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Literature Cited

(1) Barta, *Chimie et industrie*, 35, 792–6 (1936).
(2) Carlson, *Proc. Am. Soc. Testing Materials*, 34, Pt. II, 322–8 (1934).
(3) Davey, *Concrete and Constructional Eng.*, 26, 359–64 (1931).
(4) Davey and Fox, Dept. Sci. Ind. Research (Brit.), Bldg. Research, *Tech. Paper* 15 (1935).
(5) Davis and Traxell, *Proc. Am. Soc. Testing Materials*, Reprint 62, 1–19 (1931).
(6) Grozdorskaya and Yaichnikova, *Navosti Teckhniki Bureniya*, 4, No. 2, 5–6 (1936).
(7) Hemeon, Ind. Eng. Chem., 27, 694–9 (1935).
(8) Killig, *Cement*, 8, 499–501 (1919).
(9) Lees and Charlton, Handbook of Chemistry and Physics, 21st ed., p. 1358, Cleveland, Chemical Rubber Publishing Co., 1936–37.
(10) Lerch, *Eng. News-Record*, 113, 523–4 (1934).
(11) Maeda, *Bull. Inst. Phys. Chem. Research* (Tokyo), 14, 714–19 (1935).
(12) Pershke, *Chem. Zentr.*, 1931, I, 2379.
(13) Sheard, *Proc. Phys. Soc.* (London), 48, 498–512 (1936).
(14) Swietoslowski and Rosinski, *Przemysl Chem.*, 18, 590–4 (1934).
(15) Timms and Whithey, *J. Am. Concrete Inst.*, 5, 159–81 (1934).
(16) Woods, Steinour, and Starke, *Eng. News-Record*, 109, 404 (1932).

Inactive Inositol and Its Derivatives

PREPARATION AND PROPERTIES

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BARTOW and Walker (*1*) prepared inositol from the steep water obtained in the manufacture of starch from corn without the use of acids. This work was continued for the purpose of obtaining larger quantities of inositol, of improving the process of preparing inositol, of finding other sources of inositol, and of studying the preparation and properties of its derivatives.

Preparation of Inositol

Inositol was prepared by the simple method of Bartow and Walker (*1*). The raw material (obtained from Penick & Ford, Ltd.) was the precipitate made by adding lime to steep water. It had the consistency of thin paste and contained about 20 per cent of solids. A 225-kg. batch of this wet material, equivalent to 45 kg. of dry substance, was heated in a large autoclave for 10 hours under 5.6 kg. per sq. cm. steam pressure. After being heated, the material was neutralized with milk of lime (to phenolphthalein alkalinity), diluted with water to about 680 liters, then agitated, and boiled for 5 minutes by passing in steam. After the sludge settled, the supernatant liquid was removed by decantation. The sludge was diluted with water, heated with steam, and allowed to settle, and the supernatant liquid was again decanted. This process was repeated and the combined liquids from the three decantations were evaporated to a small volume in large open evaporators; they were filtered while hot to remove precipitated impurities. The inositol which crystallized out on cooling was removed by filtration, the mother liquor was further concentrated, and the residual inositol was precipitated by adding glacial acetic acid and alcohol. The average yield for the first nine experiments was 12.00 per cent of the dry matter in the material used.

A lower yield of inositol was obtained when an attempt was made to remove the liquid from the sludge by filtration. Only 10.00 per cent of inositol was obtained when the liquid was separated from the sludge by filtration on an Oliver filter. More washing on the filter should increase the yield.

Effect of pH on Yield from Precipitates. Precipitates were carefully prepared by the Clinton Company by adding milk of lime to steep water until the desired pH values were reached. Five samples precipitated at pH values ranging from 5.5 to 7.5, inclusive, gave a yield of inositol decreasing regularly as the pH increased (Table I). About 3 kg. of the precipitate (dry) were used in each of these tests. The amount of precipitate obtained from given quantities of steep water at the lower pH values is small; hence it is less practical to use material precipitated below a pH of 6.5. The precipitate obtained at the higher pH values probably contains such impurities as $CaCO_3$ or $CaHPO_4$. The crude inositol obtained at a pH of 7 or higher was very dark and impure, but a recrystallization gave good quality.

Table I. Yield of Inositol When Precipitate Was Formed at Different pH Values

Sample No.	pH	Yield of Inositol, %
11	5.5	11.94
12	6.0	10.80
13	6.5	10.14
14	7.0	8.85
15	7.5	6.25

Inositol from Wheat Bran. Wheat bran was steeped for 24 hours at 50° C. in a solution containing 0.4 per cent of hydrochloric acid. The steep water, which contained the acid-soluble portion of the bran and some starch and gluten, was drained from the bran; and after settling for several hours, the supernatant liquid was siphoned from the starch-gluten mixture. Neutralization with milk of lime to phenolphthalein alkalinity brought down an insoluble precipitate from which inositol was obtained by hydrolysis. The same procedure was used as with the precipitate from steep water obtained in the manufacture of cornstarch.

The yield of inositol from wheat bran in five experiments was relatively small—only 0.52 per cent. Bran is less satisfactory than steep water as a source of inositol. Since bran is valuable as a stock food, its use as a source of inositol can be practical only if the treated bran can still be used as feed.

Organic Esters of Inositol

Müller (*3*) prepared the hexacetyl derivative by heating inositol with an excess of acetic anhydride in the presence of zinc chloride. Griffin and Nelson (*2*) prepared inositol hexabenzoate by heating benzoyl chloride and inositol to 120° C. in the presence of quinoline.

Inositol Hexacetate, $C_6H_6(OCOCH_3)_6$, was prepared according to the method of Müller (*3*) by heating inositol with an excess of acetic anhydride in the presence of zinc chloride. The reaction proceeded without difficulty, and a pure product was obtained. The melting point was 212° C., and the yield was almost quantitative.

Inositol hexacetate was also prepared by refluxing inositol (1 gram) and an excess (5 grams) of acetyl chloride in the presence of a little zinc chloride. Without zinc chloride little or no reaction took place, but when this reagent was added, the reaction proceeded briskly without further application of heat. After recrystallization from alcohol, the white crystalline compound melted at 212° C., which is the same as that recorded by Müller (*3*).

Inositol Hexapropionate, $C_6H_6(OCOC_2H_5)_6$, was prepared by refluxing inositol with an excess of propionyl chloride for one hour in the presence of zinc chloride. When the mixture was poured into ice water, the derivative precipitated immediately. The precipitate was washed repeatedly with portions of water and finally recrystallized with alcohol. The white crystalline substance melted at 100° C. and had a molecular weight of 532.

Inositol Hexabutyrate, $C_6H_6(OCOC_3H_7)_6$, was prepared by refluxing inositol with an excess of *n*-butyryl chloride in presence of zinc chloride. After being heated for one hour, the dark colored sirupy liquid was poured into a beaker of ice water. The solid ester precipitated immediately and was separated by filtration, thoroughly washed with water, dried, and recrystallized from alcohol. It was necessary to recrystallize twice from alcohol to obtain a pure product, which melted at 81° C. and had a molecular weight of 587.

Inositol Hexaisobutyrate, $C_6H_6[OCOCH(CH_3)_2]_6$, was prepared by refluxing inositol and *sec*-butyryl chloride in the presence of zinc chloride in the manner previously described. The white crystalline product melted at 181° C. and had a molecular weight of 624.

Inositol Hexavalerate, $C_6H_6(OCOC_4H_9)_6$, and Inositol Hexaisovalerate, $C_6H_6[OCOCH_2CH(CH_3)_2]_6$, were prepared by refluxing inositol with an excess of valeryl chlorides in the presence of zinc chloride for 45 minutes on an oil bath at 120° C. In each case a brisk reaction began when a temperature of about 90° C. was reached, and much hydrochloric acid gas was evolved. After refluxing, the dark colored sirupy liquid was poured into ice water. At first no solid precipitate was formed, but instead an oily layer appeared in the bottom of the beaker which would not harden. After prolonged stirring, the dark colored oil began to crystallize. The precipitate in each case was pulverized, washed repeatedly with water, and finally filtered. Recrystallization from alcohol gave a white crystalline product in each case. Inositol hexavalerate melted at 63° C. and had a molecular weight of 668. Inositol hexaisovalerate melted at 147° C. and had a molecular weight of 697.

Table II. Melting Points and Molecular Weights of the Organic Esters

Derivative	Formula	M. P., ° C.	Mol. Weight Detd.	Mol. Weight Theoretical
Acetyl	$C_6H_6(OCOCH_3)_6$	212	...	432
Propionyl	$C_6H_6(OCOC_2H_5)_6$	100	532	516
n-Butyryl	$C_6H_6(OCOC_3H_7)_6$	81	587	600
sec-Butyryl	$C_6H_6[OCOCH(CH_3)_2]_6$	181	624	600
n-Valeryl[a]	$C_6H_6(OCOC_4H_9)_6$	63	668	684
Isovaleryl[a]	$C_6H_6[OCOCH_2CH(CH_3)_2]_6$	147	697	684
3,5-Dinitrobenzoyl	$C_6H_6[OCOC_6H_3(NO_2)_2]_6$	86	1252	1380

[a] Reaction was carried out by heating on an oil bath at 110° to 120° C. for 45 minutes.

The melting points of derivatives of the normal acids decrease as the molecular weights of the fatty acids used increase. The branched-chain acid derivatives have a higher melting point than the corresponding straight-chain acid derivatives.

Attempts to prepare derivatives of *n*-caproic, isocaproic, and *n*-capric acids have thus far been unsuccessful. In each case inositol was heated with an excess of the corresponding acid chloride in presence of a little zinc chloride. A brisk reaction took place and much hydrochloric acid gas was given off. In each case an oily substance was obtained which would not crystallize.

Inositol Hexa-3,5-dinitrobenzoate, $C_6H_6[OCOC_6H_3(NO_2)_2]_6$, was prepared by heating inositol with an excess of 3,5-dinitrobenzoyl chloride for 3 to 5 minutes over a free flame. When the mixture was poured into ice water, a solid precipitated and was recrystallized from alcohol. The molecular weight was found to be 1252 (theoretical, 1380); the melting point was 86° C.

Action of Certain Chlorides and Anhydrides. Unsuccessful attempts were made to prepare derivatives of succinic acid, phthalic acid, and the chloroacetic acids. In each case a mixture of inositol with the chlorides or anhydrides was heated with or without zinc chloride as catalyst and with or without pyridine as a solvent. Unchanged inositol was recovered except when decomposition took place.

Literature Cited

(1) Bartow, Edward, and Walker, W. W., Ind. Eng. Chem., 30, 300–3 (1938); U. S. Patent 2,112,553 (1938).
(2) Griffin, E. G., and Nelson, J., *J. Am. Chem. Soc.*, 37, 1552–71 (1915).
(3) Müller, H., *J. Chem. Soc.*, 91, 1780 (1907).

Enzyme Activity in Frozen Vegetables

STRINGBEANS[1]

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THE inactivation of the respiratory enzymes of vegetables by scalding is now well established as an essential practice in the preparation of vegetables for preservation by freezing (*3*, *5*). The heating, however, often causes profound modifications in texture, may cause the formation of undesirable cooked flavors, and may bring about the loss of desirable nutritive elements such as soluble salts and vitamins. Therefore, considerable attention has been paid to the development of scalding procedures which are adequate for the necessary destruction of the enzymes but which will result in a minimum of the undesirable changes.

There is some difference of opinion concerning the most suitable scalding temperatures and periods of exposure to be employed in producing frozen vegetables of high quality. These differences of opinion may be due to variations in the vegetables used (such as variety, maturity, freshness, or growing conditions), to the methods of the investigation, or to the different objectives of the respective investigators.

In scalding the vegetables, they should be brought quickly to the desired temperatures (usually about 210° F.) in a suitable medium (steam, water, or citric acid solution), held there for the necessary period of time, and then promptly cooled. Although some information on the thermal rate of inactivation of certain enzyme systems in several vegetables is available, and several investigations on vitamin losses in blanching have been made, all the data necessary to the selection of the best procedure of scalding vegetables is still lacking. Our knowledge of the nature of the enzyme systems involved, of the substrates acted upon, and of the products formed is still fragmentary. There is some evidence that the individual vegetables vary considerably in their response to scalding.

In the belief that an investigation of the quantitative rate of destruction of the enzymes believed to be involved in formation of off-flavors would lead to a better understanding of the process, the investigations on the relation between enzyme activity and the retention of flavor and color of vegetables stored at −17° C. (+1.4° F.) previously reported for peas and spinach (*1*) and artichoke hearts (*4*), have been continued and data have been obtained for other vegetables. In this paper the data are reported on the enzyme activity in frozen stringbeans as affected by blanching conditions.

There are no extensive investigations of the effect of scalding on the quality of string beans; the usual procedure is to blanch the beans in boiling water for 2 to 5 minutes, depending on size and maturity. The procedure used in canning is to heat the beans only to the point where they are flexible enough to pack well. According to Bitting (*2*):

> Two minutes suffice for prime Nos. 1, 2, and 3 sizes and from 3 to 4 minutes for the Nos. 4 and 5 sizes. If, however, the stock be old or the growth be arrested by dry weather, the larger sizes may require 5 or 6 minutes. Beans requiring more than 4 minutes may be made soft but not of prime quality. The almost universal practice is to blanch at a temperature between 200° and 212° F., though a somewhat lower one, about 180° to 185°, continued for a longer time, might prove preferable, especially for Nos. 1 and 2. The French use a 12 to 15 minute low-temperature blanch but do not indicate the degree used.
>
> If the pods show a tendency to soften to excess or to slough in the blanching, it has been found advantageous to use hard water, or at least this has been reported as desirable by one of the large packers. Under most circumstances, however, the better practice is to use soft water and to regulate the heat accordingly.

Preparation and Storage of Material

SERIES I. Locally grown Kentucky Wonder stringbeans of large size were trimmed and cut into 2-inch (5-cm.) lengths; after being mixed and washed, aliquots were treated (blanched) in water for 2 minutes at 20°, 40°, 50°, 60°, 65°, 70°, 75°, 77.5°, 80°, 82.5°, 85°, 87.5°, 90°, 95°, and 100° C. (68°, 104°, 122°, 140°, 149°, 158°, 167°, 171.5°, 176°, 180.5°, 185°, 189.5°, 194°, 203°, and 212° F.), respectively. The stringbeans were immersed in a 45-liter water bath in loosely tied cheesecloth bags containing approximately 1.4 kg. of stringbeans. The cheesecloth bags were sufficiently large to allow the blanching water to circulate freely over the stringbeans. The beans came to bath temperature in less than 30 seconds. Each successive lot was blanched in the same water. After being blanched, the stringbeans were rapidly cooled in running cold water, packed into 8-ounce (237-ml.) tin cans, sealed, and stored at −17° C.

Stringbeans were also blanched in water for various periods from 30 seconds to 60 minutes at 55°, 65°, and 75° C. (131°, 149°, and 167° F.), and in boiling water and in flowing steam for 15 and 30 seconds, and 1, 2, and 5 minutes, respectively. In this set of tests the quantities of stringbeans needed for the samples were tied in separate cheesecloth bags. All the bags that were to be held at a constant temperature were then immersed in a 12-gallon (45-liter) water bath; at definite prearranged intervals a bag of stringbeans was removed, cooled in running water, packed, sealed, and stored. The water in the bath was changed for each succeeding temperature interval. In addition, in order to remove air from intracellular spaces and to destroy organic peroxides, samples of stringbeans were impregnated in water, 3 per cent salt solution, 1 per cent tartaric acid, and 1 per cent hydrochloric acid solution by a process of vacuumization followed by release with air which was repeated for several cycles. The stringbeans were under the various solutions mentioned when air replaced the vacuum.

The samples for the first series of tests were prepared on June 22, 1932, and held in storage for over 4 years before analysis.

SERIES II. Freshly picked, uncut, pink-seeded, Kentucky Wonder stringbeans grown in Santa Clara County were used in the second series. The stringbeans were graded for size and snipped as for canning, the No. 2 sieve size being used. After being mixed and washed, aliquots were blanched in water at 100° C. for 1, 2, 3, 4, 5, and 6 minutes. In this set of tests the quantities of stringbeans needed for the samples were placed in Chinese bamboo baskets. The baskets were immersed in the water bath; at definite intervals a basket of stringbeans was removed, cooled in running water, packed, sealed, and stored. The bamboo baskets were filled one third full. They were very porous so that the blanching water was able to circulate freely over the aliquots of stringbeans. There was a temperature lag of 15 seconds in the center of the baskets that was taken into consideration in the blanching time.

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[1] Previous articles in this series appeared in 1936 (*1*) and 1938 (*4*).

Aliquots were also blanched in water for 5 minutes at 71.1° C. (160° F.) and 76.7° C. (170° F.), respectively, and for 3 and 5 minutes at 82.2° C. (180° F.), 87.8° C. (190° F.), and 93.3° C. (200° F.), respectively. Each successive lot was blanched in the same water. After being blanched, the stringbeans were rapidly cooled in running cold water, packed, sealed, and stored. They were frozen at −34° C. (−30° F.) in an air blast tunnel.

The above aliquots were all packed in one-quart friction-top cans and stored at −23° C. (+9.4° F.). The material was held at −23° C. for 7 months before examination.

Analytical Methods

Catalase Activity was determined as in the previous investigation (*1*) by a modification of the Balls and Hale procedure.[2] A representative sample of stringbeans (250–350 grams) was taken, and the ice crystals clinging to the external surface were removed. The sample was ground in a food chopper while frozen and was then mixed, and an 8- or 10-gram aliquot of the mixture was further triturated with approximately 10 grams of sharp quartz sand and 40 or 50 ml. of an equal mixture of 95 per cent glycerol and 0.2 *M* phosphate buffer at pH 7.0. This mixture was allowed to stand 15 minutes to allow for solution of the catalase. The aqueous portion was separated by thorough pressing through cheesecloth, and the volume of extract was determined.

An aliquot of enzyme solution (1–10 ml.), sufficient to decompose approximately half of the hydrogen peroxide solution used, was introduced into a 50-ml. volumetric flask containing 4–6 ml. of 0.2 *M* phosphate buffer (pH 7.0), approximately 1 gram of dextrose per 40 ml. of water (freshly prepared), and 1 ml. of 0.2 *N* hydrogen peroxide, and the volume was made up to 50 ml. The volumetric flask was thoroughly shaken to obtain a uniform mixture. Then a 10-ml. aliquot was removed and pipetted into a 125-ml. flask containing 20 ml. of 4 *N* sulfuric acid and 5 drops of a saturated water solution of molybdic acid. Time was taken at half delivery of pipet and is the starting time of the run. Ten milliliters of 10 per cent potassium iodide were added immediately, and the contents allowed to stand approximately 4 minutes. The iodine liberated was then titrated with 0.01 *N* sodium thiosulfate by means of a microburet. Additions of 10-ml. aliquots were removed at various time intervals.

The catalase factor is determined by the formula:

$$K = \frac{1}{t} \log \frac{a}{a - x}$$

where t = time
a = first titer value
$a - x$ = subsequent titer values

Representative titrations and corresponding K values are given in Tables I and II where K_t is the actual K value obtained and K_t/gram is the catalase factor based on grams of fresh material present in the 10-ml. aliquot used. Table I includes the ranges in volume of extract used and the titration values obtained. The reproducibility of the results obtained is shown in Table II.

Table I. Representative Data on Catalase Activity Obtained for Samples of Varying Strength

Blanching Condition Temp. ° *C.*	Blanching Condition Time *Min.*	Wt. of Sample *Grams*	Vol. of Extract *Ml.*	Aliquot Used *Ml.*	Time *Min.*	0.01 *N* Thiosulfate *Ml.*	K_t	K_t/Gram	Av. K_t/Gram
No blanch		10	50	3	0	3.60	....	....	
					5	3.06	0.0140	0.117	
					10	2.46	0.0166	0.138	
					15	2.12	0.0153	0.127	0.127
20	2	10	49	3	0	3.56	....	....	
					5	3.06	0.0132	0.108	
					10	2.57	0.0142	0.116	
					15	2.23	0.0136	0.111	0.112
40	2	10	51	5	0	3.54	....	....	
					5	2.75	0.0220	0.112	
					10	2.12	0.0223	0.114	
					15	1.68	0.0219	0.112	0.113
50	2	10	51.5	5	0	3.61	....	....	
					5	2.92	0.0184	0.095	
					10	2.42	0.0174	0.090	
					15	2.00	0.0171	0.088	0.091
60	2	10	50	5	0	3.66	....	....	
					5	3.15	0.0132	0.066	
					10	2.70	0.0132	0.066	
					15	2.40	0.0123	0.062	0.065
65	2	10	51	10	0	3.65	....	....	
					5	3.14	0.0132	0.034	
					10	2.60	0.0148	0.038	
					15	2.38	0.0124	0.032	0.035
75	0.5	8	41	10	0	3.62	....	....	
					5	3.22	0.0102	0.026	
					10	2.75	0.0119	0.030	
					15	2.44	0.0114	0.029	0.028
75	1	8	40	10	0	3.70	....	....	
					5	3.57	0.0031	0.0077	
					10	3.54	0.0020	0.0050	
					15	3.42	0.0023	0.0056	0.0061
75	2	8	41	10	0	3.70	....	....	
					5	3.66	0.0010	0.0026	
					10	3.58	0.0014	0.0036	
					15	3.58	0.0009	0.0023	0.0028
100	0.25	10	50	10	0	3.70	....	....	
					5	3.48	0.0053	0.013	
					10	3.22	0.0061	0.015	
					15	3.04	0.0057	0.014	0.014

Peroxidase Activity was determined as in the previous investigation (*1*) by a modification of the Balls procedure. A representative sample was prepared as for catalase, and a 5-gram aliquot was further triturated with approximately 10 grams of sharp quartz sand and 45 ml. of 0.1 *M* phosphate buffer of pH 8.0. This mixture was allowed to stand 15 minutes to allow for solution of the peroxidase. The aqueous portion was then separated by thorough pressing through cheesecloth into a 50-cc. graduated cylinder, and the volume of extract was determined after the larger particles had settled.

Two hundred milliliters of distilled water and 25 ml. of 0.2 *M* phosphate buffer (pH 8.0) were introduced into a 300-ml. stoppered flask, and placed in a water bath at 30° C. (86° F.) for 15 minutes. Then 2 ml. of 0.2 *N* hydrogen peroxide and 10 ml. of 6.25 per cent pyrogallol solution were added, and the contents of the flask thoroughly mixed.

Previous investigations showed that the trend of the results is the same whether the layer of mineral oil recommended by Balls is used or not. Even the omission of nitrogen to flush out the air from the flask and to stir the mixture had but little effect, although the end point in the titration was obscured by the products of autoxidation of pyrogallol. Little or no autoxidation occurred when care was taken to vacuumize the mixture in the flask, and relieve with nitrogen gas, and repeat this cycle several times. More

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[2] In the article on peas and spinach (*1*), the catalase activity was expressed, not in terms of the *k* units per gram of fresh material, but in *k* units per cc. of enzyme extract. This was prepared by grinding 4 grams of vegetable with 18 cc. of phosphate buffer, centrifuging, and adding 1 cc. of this extract to 50 cc. substrate-buffer mixture, 10-cc. aliquots of which were taken for analysis. Liver extract was not used, since preliminary tests indicated that catalase inhibitors were not present, at least in appreciable concentrations, in the peas and spinach investigated. To obtain the catalase factor in *k* units per gram, the results given should be multiplied by 5 × (18/4) or 22.5. This does not alter the trends.

TABLE II. REPRODUCIBILITY OF THE CATALASE DETERMINATION IN VARIOUS STRINGBEAN SAMPLES

Time Min.	0.01 N Thiosulfate Ml.	K_t	K_t/Gram	0.01 N Thiosulfate Ml.	K_t	K_t/Gram	0.01 N Thiosulfate Ml.	K_t	K_t/Gram	Av. K_t	Av. K_t/Gram	Av. of Preceding Column
I. Unblanched, 10 Grams per 50 Ml., 3-Ml. Aliquot												
0	3.60	....	....	3.45	....	....	3.51	....	....	....	....	
5	3.06	0.0140	0.117	2.88	0.0180	0.150	3.05	0.0124	0.103	0.0148	0.123	
10	2.46	0.0166	0.138	2.46	0.0158	0.132	2.45	0.0156	0.130	0.0160	0.133	
15	2.12	0.0153	0.127	2.05	0.0158	0.132	2.15	0.0142	0.118	0.0151	0.126	0.127
II. Unblanched, 10 Grams per 50 Ml., 3-Ml. Aliquot												
0	3.59	....	....	3.52	....	....	3.65	....	....	....	....	
5	2.86	0.0198	0.165	2.89	0.0172	0.143	2.98	0.0176	0.147	0.0182	0.152	
10	2.40	0.0174	0.145	2.35	0.0176	0.147	2.34	0.0193	0.161	0.0181	0.151	
15	1.91	0.0183	0.153	2.00	0.0164	0.137	2.06	0.0166	0.138	0.0171	0.143	0.148
III. Unblanched, 10 Grams per 51 Ml., 3-Ml. Aliquot												
0	3.64	....	....	3.60	....	....	..	....	....	....	....	
5	3.06	0.0152	0.130	3.02	0.0152	0.130	..	....	....	0.0152	0.130	
10	2.50	0.0163	0.139	2.50	0.0158	0.135	..	....	....	0.0160	0.137	
15	2.24	0.0141	0.120	2.14	0.0151	0.129	..	....	....	0.0146	0.124	0.130
Blanched 4 Minutes at 55° C., 8 Grams per 41 Ml., 3-Ml. Aliquot												
0	4.34	....	....	4.32	....	....	..	....	....	....	....	
2	4.12	0.0110	0.094	4.10	0.0115	0.098	..	....	....	0.0112	0.096	
5	3.77	0.0120	0.103	3.76	0.0120	0.103	..	....	....	0.0120	0.103	
7	3.53	0.0127	0.108	3.55	0.0123	0.105	..	....	....	0.0125	0.106	0.102
Blanched 4 Minutes at 55° C., 8 Grams per 41.5 Ml., 3-Ml. Aliquot												
0	4.41	....	....	4.44	....	....	..	....	....	....	....	
2	4.19	0.0120	0.104	4.17	0.0130	0.113	..	....	....	0.0125	0.108	
5	3.89	0.0110	0.096	3.86	0.0120	0.104	..	....	....	0.0115	0.100	
7	3.65	0.0120	0.104	3.68	0.0116	0.101	..	....	....	0.0118	0.102	0.103
Blanched 1 Minute at 75° C., 8 Grams per 41 Ml., 10-Ml. Aliquot												
0	3.70	....	....	3.81	....	....	3.90	....	....	....	....	
5	3.76	....	....	3.84	....	....	3.86	0.0010	....	....	....	
10	3.50	0.0024	0.0061	3.50	0.0037	0.0095	3.63	0.0032	0.0082	0.0031	0.0079	
15	3.50	0.0016	0.0041	3.54	0.0021	0.0054	3.61	0.0022	0.0056	0.0019	0.0050	0.0064
Blanched 1 Minute at 75° C., 8 Grams per 40 Ml., 10-Ml. Aliquot												
0	3.70	....	....	3.64	....	....	3.68	....	....	....	....	
5	3.57	0.0031	0.0079	3.62	....	....	3.56	0.0029	0.0072	0.0030	0.0074	
10	3.54	0.0020	0.0050	3.48	0.0020	0.0050	3.45	0.0028	0.0070	0.0023	0.0057	
15	3.42	0.0022	0.0055	3.38	0.0022	0.0055	3.47	0.0017	0.0042	0.0020	0.0051	0.0060

readily reproducible results were obtained with this technique. However, for the most part the determinations reported in this paper were made without these precautions.

An aliquot of enzyme solution (1–10 ml.) that does not decompose more than one third of the hydrogen peroxide added was then introduced, and the contents of the flask again thoroughly mixed. A 25-ml. aliquot was removed and placed in a 125-ml. flask containing 0.5 gram of pyrogallol per 25 ml. of 2 N sulfuric acid. Time was taken at half delivery of the pipet and is the starting time of the run. Then 10 ml. of 10 per cent potassium iodide were added, and the flask was allowed to stand 12–14 minutes. The liberated iodine was titrated with 0.01 N thiosulfate by means of a microburet. Additional 25-ml. aliquots were taken at time intervals of 2, 5, 7, 10, and 15 minutes.

From the titrations the peroxidase units are calculated on terms of the purpurogallin number of Willstätter, milligrams of purpurogallin produced by 1 mg. of enzyme material in 5 minutes, as follows:

$$P.E. = 0.00184 \frac{a - x}{t}$$

where a = initial titration of 0.01 N thiosulfate at 0 min., ml.
x = titration of 0.01 N thiosulfate at time t, ml.
$P.E.$ = peroxidase units in aliquot used for the titration—namely, 1/10 of total enzyme used

It is convenient to express peroxidase quantities as $P.E.$ per gram, since the number of units per gram is also the purpurogallin number.

Representative titrations and corresponding $P.E.$ values are given in Tables III and IV. As in the case of artichokes (*4*), the $P.E.$ values in Table III markedly decreased with time in the more active samples, although substantially constant values were obtained for the weaker preparations. As Table IV shows, the trends in most cases were quite reproducible with only an occasional erratic result.

The determinations of catalase and of peroxidase activity were made in triplicate, and only the average of closely agreeing duplicates is given in the subsequent tables.

ASCORBIC ACID OXIDASE ACTIVITY was determined as for artichokes in the following way (*4*): A 10-gram sample was ground with sand and 50 ml. of water. To a 5-ml. aliquot of the extract were added 40 ml. of 8 per cent sulfuric acid and then 1 ml. of an ascorbic acid solution containing 0.5 mg. of ascorbic acid per ml.; the mixture was titrated at once with 0.01 N iodine solution with starch indicator. Another 5-ml. aliquot of the extract was heated for 5 minutes at 100° C., cooled, mixed with 1 ml. of ascorbic acid solution and stored at room temperature for 15 minutes. It was then acidified and titrated as above. A third aliquot was treated with 1 ml. of ascorbic acid solution, allowed to stand for 15 minutes, and acidified and titrated as above.

ACETALDEHYDE was determined by the direct iodometric sulfite procedure used previously (*1*, *4*).

Organoleptic Observations

SERIES I. Samples of the canned frozen material were removed from freezing storage and observed for color, odor, texture, and flavor before and after cooking. These samples

Table III. Representative Data on Peroxidase Values Obtained from Preparations of Various Strengths

Blanching Condition								
Temp. ° *C.*	Time *Min.*	Wt. of Sample *Grams*	Vol. of Extract *Ml.*	Aliquot Used *Ml.*	Time *Min.*	0.01 *N* Thiosulfate *Ml.*	$\frac{a-x}{t}$	*P.E.*/Gram × 10⁻²
No blanch		5	46	2	0	4.42	...	...
					2	4.08	0.170	1.44
					5	3.64	0.156	1.32
					7	3.49	0.133	1.12
					10	3.30	0.112	0.95
					15	3.03	0.092	0.78
20	2	5	50	3	0	4.60	...	...
					2	4.08	0.260	1.58
					5	3.63	0.194	1.19
					7	3.39	0.173	1.06
					10	3.16	0.144	0.88
					15	2.74	0.124	0.76
50	2	5	50	3	0	4.72	...	...
					2	4.29	0.215	1.32
					5	3.90	0.164	1.00
					7	3.66	0.151	0.92
					10	3.48	0.124	0.76
					15	3.16	0.104	0.64
65	2	5	50	3	0	4.49	...	...
					2	4.06	0.215	1.32
					5	3.60	0.178	1.09
					7	3.40	0.155	0.95
					10	3.14	0.135	0.83
					15	2.86	0.108	0.66
75	2	5	50	5	0	4.47	...	...
					2	4.05	0.210	0.77
					5	3.59	0.176	0.65
					7	3.38	0.155	0.57
					10	3.10	0.137	0.50
					15	2.81	0.110	0.40
77.5	2	5	50	5	0	4.46	...	...
					2	4.20	0.120	0.48
					5	3.80	0.132	0.49
					7	3.56	0.128	0.47
					10	3.30	0.116	0.43
					15	3.03	0.095	0.35
80	2	5	50	5	0	4.67	...	...
					2	4.49	0.090	0.33
					5	4.21	0.092	0.34
					7	4.04	0.090	0.33
					10	3.86	0.081	0.30
					15	3.52	0.076	0.28
85	2	5	50	5	0	4.56	...	...
					2	4.43	0.065	0.24
					5	4.25	0.062	0.23
					7	4.17	0.055	0.20
					10	3.98	0.058	0.21
					15	3.60	0.064	0.24
87.5	2	5	50	5	0	4.62	...	...
					2	4.61	0.005	0.018
					5	4.60	0.004	0.015
					7	4.57	0.007	0.026
					10	4.56	0.006	0.022
					15	4.35	0.018	0.067

were observed organoleptically 3 and 6 months after storage and at the time of analyses. They were cooked in a boiling one per cent sodium chloride solution for 15 minutes. In the samples of stringbeans blanched at a constant time of 2 minutes, those below 77.5° C. had a good green color; those between 77.5° and 82.5° C. were brownish to a dull olive green. At 85° C. and above they had the characteristic green color of properly blanched stringbeans. When cooked, the 82.5° C. sample and those below turned olive green whereas the samples at 85° C. and above retained the green color. Texture changes occurred in samples blanched at 85° and at 90° C. Those blanched below 85° C. were tough and those at 90°, 95°, and 100° C. were mushy and soft when cooked; these qualities increased with temperature. Noticeable differences in flavor and odor occurred in the ranges of temperature from 20° to 80°, 82.5 to 90°, and 95° to 100° C. Before and after cooking, the odor and flavor of the samples blanched in the temperature range 20° to 80° C. were decidedly alfalfalike and disagreeable. This odor and flavor decreased in intensity as the temperature of blanching increased. The sample blanched at 82.5° C. had a slight off-flavor and those at 85°, 87.5°, and 90° C. had a fairly agreeable odor and flavor. At 95° and 100° C. there was no off-odor, but the samples were insipid and had lost their stringbean flavor.

Series II. Before and after cooking, the odor and flavor of the samples blanched at 71.1° and 76.7° C. for 5 minutes were decidedly haylike and disagreeable. The samples blanched at 100° C. for 1 minute and at 82.2° C. for 3 minutes had a slight off-flavor but no off-odor. The other samples all had an agreeable odor and flavor, but those blanched at 100° C. began to lose their flavor when blanched longer than 3 minutes.

The color of the sample blanched for 1 minute at 100° C. was dull grayish green, but all other samples had the characteristic green color of properly blanched stringbeans.

The samples blanched at 100° C. for 3, 4, 5, and 6 minutes, and at 87.8° and 93.3° C. for 3 and 5 minutes, respectively, were decidedly mushy in texture and sloughy when cooked; these qualities increased with temperature and length of blanching period.

Data and Discussion

As Table V shows the catalase activity in cut stringbeans heated for 2 minutes at various temperatures rapidly decreased with increase in temperature of blanching and was practically absent in samples blanched at 75° C. The acetaldehyde content also decreased with increase in temperature and paralleled the decrease in catalase activity; this tendency indicated that anaerobic respiration processes were closely related to production of off-flavors as was found previously for peas (*1*). However the flavor of the stringbeans scalded just long enough to inactivate catalase was poor, although in this lot of stringbeans all samples were below the average market quality because of the long storage period. Apparently the catalase of these stringbeans was inactivated at temperatures below those necessary to inactivate the enzyme systems, and off-flavors resulted. As in the case of peas, heating to temperatures necessary to inactivate the agencies responsible for spoilage also resulted in retention of green color. Thus the color of stringbeans heated at temperatures below 85° C. browned. Scalding either rendered the chlorophyll in the chloroplasts more resistant to decomposition (principally to pheophytin) or reduced the acid concentration in the cell sap. Investigations on the transformation of chlorophyll on scalding are under way and will be reported elsewhere.

The data on the effect of period of blanching at various temperatures on catalase activity is shown in Table VI. As the temperature increased, the rate of inactivation of catalase increased also. As in the case of peas, blanching in water was more uniform and resulted in more rapid inactivation of catalase. Here too the samples in which the catalase was just inactivated were definitely off flavor. Temperatures higher or times longer than those necessary to inactivate catalase are required to inactivate the agencies responsible for production of off-flavors. The aldehyde content of the corresponding samples is shown in Table VI. The constant level reached in the samples heated at 55° C. is considerably higher than that found before and does not show as regular a decrease with decrease in catalase activity as was found for

TABLE IV. REPRODUCIBILITY OF PEROXIDASE ACTIVITY DETERMINATIONS

Time Min.	0.01 N Thiosulfate Ml.	$\frac{a-x}{t}$	P.E./Gram $\times 10^{-2}$	0.01 N Thiosulfate Ml.	$\frac{a-x}{t}$	P.E./Gram $\times 10^{-2}$	0.01 N Thiosulfate Ml.	$\frac{a-x}{t}$	0.01 N Thiosulfate Ml.	Av. $\frac{a-x}{t}$	Av. P.E./Gram $\times 10^{-2}$
Unblanched, 5 Grams per 46 Ml., 2-Ml. Aliquot											
0	4.42	...	..	4.48	...	..	4.44	...	..	...	..
2	4.08	0.170	1.44	4.12	0.180	1.52	4.00	0.220	1.86	0.190	1.61
5	3.64	0.156	1.32	3.70	0.156	1.32	3.68	0.152	1.29	0.155	1.31
7	3.49	0.133	1.12	3.60	0.125	1.06	3.54	0.130	1.10	0.130	1.10
10	3.30	0.112	0.95	3.34	0.112	0.95	3.37	0.107	0.93	0.110	0.93
15	3.03	0.092	0.78	3.20	0.085	0.72	3.20	0.083	0.74	0.087	0.74
Unblanched, 5 Grams per 47 Ml., 2-Ml. Aliquot											
0	4.30	...	..	4.34	...	..	..	...	..	...	..
2	3.90	0.200	1.74	3.97	0.185	1.60	..	...	..	0.192	1.66
5	3.54	0.152	1.32	3.57	0.154	1.33	..	...	..	0.153	1.32
7	3.38	0.131	1.13	3.41	0.133	1.15	..	...	..	0.132	1.14
10	3.19	0.111	0.96	3.22	0.112	0.97	..	...	..	0.111	0.96
15	3.07	0.082	0.71	3.06	0.085	0.74	..	...	..	0.083	0.72
Can 1, Blanched 2 Min. at 55° C., 5 Grams per 49 Ml., 5-Ml. Aliquot											
0	4.60	...	..	4.81	...	..	..	...	..	...	..
2	4.18	0.210	0.77	4.45	0.180	0.65	..	...	..	0.195	0.71
5	3.76	0.168	0.61	4.00	0.162	0.58	..	...	..	0.165	0.59
7	3.52	0.154	0.56	3.81	0.143	0.52	..	...	..	0.148	0.54
10	3.30	0.130	0.47	3.64	0.117	0.42	..	...	..	0.123	0.44
15	3.18	0.095	0.34	3.52	0.086	0.31	..	...	..	0.090	0.32
Can 1, Blanched 2 Min. at 55° C., 5 Grams per 50 Ml., 5-Ml. Aliquot											
0	4.08	...	..	4.40	...	..	..	...	..	...	..
2	3.65	0.215	0.79	4.00	0.200	0.74	..	...	..	0.207	0.76
5	3.15	0.186	0.68	3.48	0.186	0.68	..	...	..	0.186	0.68
7	2.91	0.167	0.61	3.29	0.158	0.58	..	...	..	0.162	0.59
10	2.70	0.138	0.51	3.04	0.138	0.51	..	...	..	0.138	0.51
15	2.46	0.108	0.40	2.77	0.108	0.40	..	...	..	0.108	0.40
Can 2, Blanched 2 Min. at 55° C., 5 Grams per 48 Ml., 2-Ml. Aliquot											
0	4.30	...	..	4.35	...	..	4.42	...	..	...	..
2	3.91	0.195	1.72	3.97	0.190	1.68	4.06	0.180	1.59	0.188	1.66
5	3.51	0.158	1.40	3.56	0.158	1.40	3.59	0.166	1.47	0.161	1.42
7	3.35	0.135	1.19	3.39	0.137	1.21	3.42	0.143	1.26	0.138	1.22
10	3.19	0.111	0.98	3.20	0.115	1.02	3.22	0.120	1.06	0.115	1.02
15	2.85	0.096	0.85	2.90	0.096	0.85	..	...	..	0.096	0.85
Can 2, Blanched 2 Min. at 55° C., 5 Grams per 48 Ml., 2-Ml. Aliquots											
0	4.57	...	..	4.59	...	..	..	...	..	...	..
2	4.22	0.175	1.54	4.29	0.150	1.32	..	...	..	0.162	1.43
5	3.90	0.134	1.18	3.94	0.130	1.15	..	...	..	0.132	1.16
7	3.80	0.110	0.97	3.78	0.114	1.01	..	...	..	0.112	0.99
10	3.66	0.091	0.80	3.66	0.093	0.82	..	...	..	0.092	0.81
15	3.52	0.070	0.62	3.51	0.072	0.64	..	...	..	0.071	0.63
Can 2, Blanched 2 Min. at 55° C., 5 Grams per 47.5 Ml., 2-Ml. Aliquot											
0	4.70	...	..	4.70	...	..	..	...	..	...	..
2	4.33	0.185	1.62	4.33	0.185	1.62	..	...	..	0.185	1.62
5	3.96	0.148	1.30	4.00	0.140	1.22	..	...	..	0.144	1.26
7	3.81	0.127	1.11	3.84	0.123	1.08	..	...	..	0.125	1.09
10	3.66	0.104	0.91	3.68	0.102	0.89	..	...	..	0.103	0.90
15	3.46	0.082	0.72	3.37	0.088	0.77	..	...	..	0.085	0.74

TABLE V. EFFECT OF BLANCHING TEMPERATURE ON CATALASE AND ACETALDEHYDE CONTENTS (SERIES I)

Temp. ° C.	Catalase Factor	Acetaldehyde P. p. m.	Temp. ° C.	Catalase Factor	Acetaldehyde P. p. m.
No blanch	0.134	28.44	65	0.033	9.6
20	0.111	25.00	75	0.000	9.6
40	0.115	24.20	77.5	...	8.8
50	0.091	22.80	80	...	5.2
60	0.067	15.80	82.5–100	...	3.5–4.8

TABLE VI. EFFECT OF BLANCHING TIME ON CATALASE AND ACETALDEHYDE CONTENTS (SERIES I)

Blanching Time	Catalase Factor at Blanching Temp. of:					Acetaldehyde Content at Blanching Temp. of:				
	55° C.	65° C.	75° C.	100° C. (H_2O)	100° C. (steam)	55° C.	65° C.	75° C.	100° C. (H_2O)	100° C. (steam)
Min.						P. p. m.				
No blanch	0.209	...	...	...	....	..	..	..	7.92	14.6
0.25	...	...	...	0.014	0.028	24.2	33.9	13.0	4.40	7.4
0.5	0.152	0.085	0.028	0.000	0.0076	24.6	17.6	8.2	3.96	3.0
1	0.125	0.055	0.006	...	0.000	42.2	11.0	8.0	3.96	3.4
2	0.114	0.027	0.002	...	....	48.0	9.2	6.8	..	..
4	0.106	0.013	0.000	...	....	..	..	..	5.72	3.0
6	0.087	0.011	...	...	....	41.4	9.6	5.2	..	..
8	0.072	0.005	...	...	....	41.0	9.2	6.0	..	..
10	0.072	0.003	...	...	....	30.8	7.4	7.4	..	..
15	0.039	0.000	...	...	....	30.8	9.6	7.2	..	..
20	0.034	...	...	...	....	26.4	9.6	5.0	..	..
30	0.024	...	...	...	....	22.0	..	8.8	..	..
60	0.009	...	...	...	....	19.8	9.2	8.8	..	..

the samples blanched for 2 minutes at various temperatures. At 65° C. and at higher temperatures the acetaldehyde content was smaller and decreased more regularly with decrease in catalase content. The relatively incomplete inactivation by steam at short intervals as compared with boiling water is apparent also.

The data presented in Table VII shows that, as previously found for peas, impregnation with salt or tartaric acid reduced catalase activity but did not destroy it, whereas impregnation with hydrochloric acid inactivated it. However the aldehyde content of the hydrochloric-acid-treated beans was as high as that for the tartaric-acid-treated samples. Again the decrease in acetaldehyde content followed the decrease in catalase only qualitatively. On the assumption that this acetaldehyde was formed by anaerobic respiration, the inactivation of the respiratory enzymes occurs somewhat more slowly than that of catalase. However, regeneration of heat-inactivated enzyme systems and the formation of acetaldehyde by the injured tissues prior to treatment may be involved also.

TABLE VII. EFFECT OF DEAERATION IMPREGNATION ON CATALASE AND ACETALDEHYDE CONTENT (SERIES I)

Impregnating Agent	Catalase Factor	Acetaldehyde *P. p. m.*
H_2O	0.091	40.0
NaCl, 3%	0.039	33.8
Tartaric acid, 1%	0.018	20.6
HCl, 1%	0.000	25.0

TABLE VIII. EFFECT OF TEMPERATURE AND TIME OF BLANCHING ON CATALASE AND ACETALDEHYDE CONTENT (SERIES II)

Temp. *° C.*	Blanching Time *Min.*	Catalase Factor	Acetaldehyde *P. p. m.*	Temp. *° C.*	Blanching Time *Min.*	Catalase Factor	Acetaldehyde *P. p. m.*
No blanch		0.447	28.60	93.3	3	....	6.16
71.1	5	0.0087	11.00	93.3	5	....	4.84
76.6	5	0.0000	8.36	100	1	0.0045	3.96
82.2	3	....	11.88	100	2	0.0000	3.96
82.2	5	....	3.96	100	3	....	4.84
87.8	3	....	3.96	100	4	....	3.08
87.8	5	....	3.96	100	5	....	2.20

TABLE IX. EFFECT OF BLANCHING TEMPERATURE ON PEROXIDASE ACTIVITY (SERIES I)

Reaction Time *Min.*	20° C.	40° C.	50° C.	60° C.	65° C.	75° C.	77.5° C.	80° C.	82.5° C.	85° C.	87.5° C.
	P.E. per gram × 10^{-2}										
2	1.50	1.44	1.32	1.54	1.34	0.79	0.47	0.31	0.21	0.21	0.018
5	1.19	1.19	1.02	1.19	1.10	0.66	0.50	0.33	0.25	0.22	0.014
7	1.08	0.99	0.93	1.02	0.94	0.57	0.44	0.32	0.25	0.19	0.022
10	0.88	0.85	0.76	0.87	0.81	0.51	0.40	0.29	0.23	0.21	0.018
15	0.73	0.70	0.69	0.71	0.67	0.41	0.35	0.26	0.23	0.24	...

TABLE X. EFFECT OF BLANCHING TIME ON PEROXIDASE ACTIVITY (SERIES I)

Time of Reaction with H_2O_2 and Pyrogallol	Peroxidase Activity, *P.E.* per Gram × 10^{-2} 0.5 min.	1 min.	2 min.	4 min.	6 min.	8 min.	10 min.	15 min.	20 min.	30 min.	60 min.
	Temperature, 55° C.										
2	1.44	1.45	1.63	1.29	1.29	1.15	1.11	0.94	0.94	0.79	0.69
5	1.24	1.20	1.38	1.06	1.02	0.96	0.96	0.81	0.85	0.72	0.62
7	1.07	1.03	1.12	0.92	0.88	0.81	0.83	0.72	0.75	0.62	0.54
10	0.90	0.84	0.93	0.77	0.70	0.67	0.69	0.62	0.64	0.53	0.44
15	0.69	0.67	0.76	0.60	0.57	0.53	0.54	0.49	0.49	0.41	0.36
	Temperature, 65° C.										
2	1.32	1.06	0.83	0.78	0.90	0.87	0.84	0.69	0.74	0.69	0.59
5	1.09	0.91	0.69	0.68	0.77	0.77	0.72	0.66	0.67	0.63	0.54
7	0.93	0.81	0.62	0.60	0.68	0.68	0.62	0.60	0.60	0.55	0.49
10	0.77	0.69	0.52	0.51	0.58	0.57	0.53	0.54	0.51	0.47	0.42
15	0.60	0.54	0.42	0.42	0.48	0.46	0.41	0.41	0.41	0.36	0.35
	Temperature, 75° C.										
	0.5 min.	1 min.	2 min.	4 min.	10 min.	12 min.	14 min.	16 min.	18 min.	20 min.	30 min.
2	1.03	1.02	0.59	0.20	0.13	0.19	0.18	0.12	0.17	0.19	0.07
5	0.84	0.83	0.47	0.26	0.19	0.21	0.27	0.18	0.20	0.20	0.13
7	0.72	0.71	0.44	0.24	0.18	0.21	0.25	0.18	0.22	0.18	0.13
10	0.59	0.62	0.37	0.22	0.17	0.18	0.24	0.18	0.21	0.18	0.14
15	0.48	0.51	0.37	0.26	0.18	0.23	0.21	0.18	0.18	0.22	0.18
	100° C. (H_2O) 0.25 min.	0.5 min.	100 ° C. (Steam) 0.25 min.	0.5 min.							
2	0.35	0.04	0.81	0.39							
5	0.32	0.04	0.64	0.36							
7	0.29	0.03	0.58	0.32							
10	0.27	..	0.49	0.27							
15	0.25	..	0.46	0.25							

TABLE XI. EFFECT OF IMPREGNATION DEAERATION ON PEROXIDASE ACTIVITY (SERIES I)

Reaction Time *Min.*	H_2O	3% NaCl	1% Tartaric Acid	1% HCl
	P.E. per gram × 10^{-2}			
2	1.47	1.62	1.37	Negative
5	1.01	1.32	1.04	
7	0.86	1.11	0.88	
10	0.69	0.94	0.70	
15	0.57	0.79	0.57	

Similar results were found for the uncut beans of series II as reported in Table VIII. The enzyme activity of the beans in this series was considerably higher than that found for series I. The beans in this series were less mature than the others and also were uncut and probably required a longer heating period to reach the same internal temperature. Here again the samples in which the catalase was just inactivated developed off-flavors so that inactivation of catalase could not be used as an index of the inactivation of the agencies responsible for production of off-flavors.

The peroxidase activity of the cut stringbeans heated for 2 minutes at various temperatures is shown in Table IX. No peroxidase activity was found in the samples heated at 90° C. and above. It is evident from the data present (in spite of the confusion caused by decrease in peroxidase values with reaction time) that the inactivation of peroxidase corresponds more closely to inactivation of the off-flavor-producing agencies than is true for catalase.

Similar results were obtained in samples of vegetables heated for various temperatures, as shown in Table X. The results on the samples treated with various solutions (Table XI) indicate that neither salt nor tartaric acid had any noticeable effect on peroxidase activity although both markedly reduced the activity of catalase. If anything, salt increased the peroxidase activity. Hydrochloric acid, however, inactivated the peroxidase.

The data for the peroxidase activity in uncut beans of series II heated under varying conditions is given in Table XII. Here the correlation between peroxidase activity and flavor retention is not so good, for samples with a *P.E.* value of about 1 × 10^{-2} unit per gram of sample were of acceptable quality. Apparently complete inactivation was not necessary in this case.

The quantitative data for peroxidase may be compared with the qualitative data on the defrosted samples as given in Table XIII. Apparently the cut stringbeans contained an enzyme system capable of bluing guaiacum directly. However, this system was rapidly inactivated by heat and was present in samples heated to 65° C. for 2 minutes in one series. However, positive tests were obtained for the oxidase system in samples heated at 65° C. for 60 minutes in another. It was definitely destroyed in samples heated 30 seconds at 75° C. and 30 seconds in steam and in boiling water. The enzyme system bluing guaiacum in the presence of hydrogen peroxide was destroyed only when the samples were heated at temperatures above 85° C. for 2 minutes. The peroxidase bluing benzidine, however, was not inactivated even at 100° C. after 5 minutes. The quantitative data presented in Table IX are more in line with the guaiacum peroxidase inactivation. The qualitative tests for catalase in stringbean of series I are in line with the quantitative data obtained previously.

The qualitative data for the uncut beans in Table XIII (Series II) indicate again the presence of a very thermolabile oxidase, a particularly thermostable benzidine peroxidase, and a moderately thermolabile guaiacum peroxidase. The inactivation of the latter follows more closely the destruction of the agencies responsible for off-flavor formation.

The amount of added ascorbic acid destroyed by the ascorbic acid oxidase of the stringbeans and by the metals and

Table XII. Effect of Temperature and Time of Blanching on Peroxidase Acidity (Series II)

Reaction Time	No Treatment	71.1° C., 5 Min.	76.7° C., 5 Min.	82.2° C. 3 min.	82.2° C. 5 min.	87.8° C. 3 min.	87.8° C. 5 min.	93.3° C., 3 Min.[a]	100° C., 1 Min.[b]
Min.	P.E. per gram × 10⁻²								
2	8.22	2.95	0.99	0.93	0.81	0.38	0.06	0.07	0.15
5	5.55	2.45	0.98	0.84	0.73	0.37	0.08	0.05	0.12
7	4.60	2.10	0.90	0.78	0.67	0.31	0.07	0.05	0.09
10	3.60	1.78	0.81	0.70	0.59	0.28	0.06	0.04	0.08
15	2.78	1.37	0.67	0.58	0.48	0.23	0.05	0.03	0.07

[a] Two other runs were negative.
[b] Runs at 2 minutes were negative.

Table XIII. Relative Enzyme Activity in Stringbeans

Effect of Temp. of Blanching for 2 Min. (Series I)

Temp.	Oxidase (Gum Guaiacum)	Peroxidase: Gum guaiacum + H_2O_2	Peroxidase: Benzidine + H_2O_2	Catalase
° C.				
20	+++	++++	++++	+++
40	+	+++	++++	+++
65	......	+++	++++	+
77.5	......	+++	++++	......
80	......	+++	++++	......
82.5	......	+++	++++	......
85	......	+	++++	......
87.5	......	......	++++	......
90	......	......	++++	......
100	......	......	+++	......

Effect of Time of Blanching (Series I)

Temp. of Blanching	Time of Blanching	Oxidase (Gum Guaiacum)	Peroxidase: Gum guaiacum + H_2O_2	Peroxidase: Benzidine + H_2O_2	Catalase
° C.					
55	30 sec.	++++	++++	++++	++++
	4 min.	++++	++++	++++	++++
	60 min.	++	++++	++++	+++
65	30 sec.	++++	++++	++++	++++
	60 min.	+++	+++	+++	+++
75	30 sec.	......	++++	++++	++
	10 min.	......	+++	++++	......
	30 min.	......	+++	++++	......
100 (boiling water)	1 min.	......	......	++	......
	2 min.	......	......	++	......
100 (steam)	15 sec.	++	++	++++	++
	30 sec.	......	++	+++	......
	1 min.	......	......	++	......
	5 min.	......	......	++	......

Effect of Time of Blanching (Series II)

Temp. of Blanching	Time of Blanching	Oxidase (Gum Guaiacum)	Peroxidase: Gum guaiacum + H_2O_2	Peroxidase: Benzidine + H_2O_2	Catalase
71.1	5 min.	++	++++	+++	+++
76.7	5 min.	......	++++	+++	+
82.2	3 min.	......	++++	+++	+
	5 min.	......	++++	+++	+
87.8	3 min.	......	+++	+++	+
	5 min.	......	+++	+++	+
93.3	3 min.	......	++	+++	+
	5 min.	......	++	+	......
100	1 min.	......	......	+++	......
	2 min.	......	......	++	......
	3 min.	......	......	++	......
	4 min.	......	......	++	......
	5 min.	......	......	......	......

other thermostable catalysts present is shown in Tables XIV to XVII. In these tables *a* is the total ascorbic acid content calculated from the initial titration, *b* is the value obtained after storage for 15 minutes in the presence of heated inactivated enzyme extract, and *c* is the value obtained after storage for 15 minutes in the presence of the active enzyme extract. As was the case with artichoke heart extracts, the loss of ascorbic acid caused by thermostable catalysts was small (about 0.05 mg. per gram of tissue added). The data in Table XIV show that the ascorbic acid oxidase is practically inactivated on heating at 75° C. for 2 minutes, as was the case for catalase (Table V). The data presented in the other tables show that the ascorbic acid oxidase of stringbeans is inactivated at nearly the same rate as the catalase. Impregnation with salt and tartaric acid, however, as well as with hydrochloric acid inactivated this oxidase (Table XVI).

The ascorbic acid oxidase activity for the uncut immature beans also followed closely the inactivation of catalase (compare Tables VIII and XVII).

Summary and Conclusions

The activity of catalase, peroxidase, and ascorbic acid oxidase, and the acetaldehyde content of stringbeans scalded

Table XIV. Effect of Temperature of Blanching for 2 Minutes on Ascorbic Acid Oxidase Activity

Temp.	Ascorbic Acid Present: Unheated control, *a*	Ascorbic Acid Present: Heated control, *b*	Ascorbic Acid Present: Untreated, *c*	Ascorbic Acid Destroyed in 15 Min.: *a-c*	Ascorbic Acid Destroyed in 15 Min.: *b-c*	Ascorbic Acid Destroyed in 15 Min.: *a-b*
° C.	Mg. per gram					
20	0.55	0.46	0.30	0.25	0.16	0.09
40	0.53	0.46	0.32	0.21	0.14	0.07
50	0.54	0.46	0.38	0.16	0.08	0.08
60	0.51	0.45	0.31	0.20	0.14	0.06
65	0.46	0.41	0.33	0.13	0.08	0.05
75	0.44	0.39	0.36	0.08	0.03	0.05
77.5	0.47	0.41	0.39	0.08	0.02	0.06
80	0.47	0.43	0.42	0.05	0.01	0.04

Table XV. Effect of Blanching Time on Ascorbic Acid Oxidase Activity (Series I)

Time	Ascorbic Acid Present: Unheated control, *a*	Ascorbic Acid Present: Heated control, *b*	Ascorbic Acid Present: Untreated, *c*	Ascorbic Acid Destroyed in 15 Min.: *a-c*	Ascorbic Acid Destroyed in 15 Min.: *b-c*	Ascorbic Acid Destroyed in 15 Min.: *a-b*
Min.	Mg. per gram					
Temperature, 55° C.						
0.5	0.46	0.40	0.32	0.14	0.08	0.06
1	0.46	0.40	0.32	0.14	0.08	0.06
2	0.46	0.38	0.25	0.21	0.13	0.08
4	0.44	0.36	0.25	0.20	0.12	0.08
6	0.48	0.42	0.29	0.18	0.13	0.05
8	0.48	0.43	0.33	0.15	0.10	0.05
10	0.49	0.44	0.33	0.16	0.11	0.05
15	0.47	0.40	0.28	0.18	0.11	0.07
20	0.48	0.40	0.29	0.18	0.10	0.08
30	0.48	0.40	0.32	0.15	0.08	0.07
60	0.42	0.41	0.36	0.07	0.06	0.01
Temperature, 65° C.						
0.5	0.49	0.43	0.30	0.19	0.13	0.06
1	0.49	0.40	0.29	0.20	0.11	0.09
2	0.50	0.41	0.34	0.16	0.07	0.09
4	0.48	0.41	0.38	0.09	0.03	0.07
6	0.49	0.40	0.36	0.13	0.04	0.09
8	0.49	0.43	0.40	0.09	0.03	0.06
10	0.49	0.41	0.38	0.11	0.03	0.08
15	0.49	0.43	0.40	0.09	0.03	0.06
20	0.49	0.42	0.40	0.09	0.02	0.07
Temperature, 75° C.						
0.5	0.46	0.42	0.30	0.16	0.12	0.04
1	0.46	0.40	0.36	0.10	0.04	0.06
2	0.46	0.40	0.36	0.10	0.04	0.06
4	0.45	0.38	0.36	0.09	0.02	0.07
10	0.45	0.40	0.38	0.07	0.02	0.05
12	0.46	0.42	0.40	0.06	0.02	0.04
Temperature, 100° C.(Steam)						
0.25	0.48	0.44	0.40	0.08	0.04	0.04
0.50	0.46	0.41	0.40	0.06	0.01	0.05
1	0.47	0.41	0.42	0.05	..	0.05
Temperature, 100° C. (Boiling Water)						
0.25	0.44	0.42	0.39	0.05	0.03	0.02
0.50	0.44	0.40	0.39	0.05	0.01	0.04
1	0.47	0.41	0.39	0.08	0.02	0.06
2	0.45	0.40	0.40	0.05	0.00	0.05

Table XVI. Effect of Impregnation Deaeration on Ascorbic Acid Oxidase Activity (Series I)

Treatment	Ascorbic Acid Present: Unheated control, *a*	Ascorbic Acid Present: Heated control, *b*	Ascorbic Acid Present: Untreated, *c*	Ascorbic Acid Destroyed in 15 Min.: *a-c*	Ascorbic Acid Destroyed in 15 Min.: *b-c*	Ascorbic Acid Destroyed in 15 Min.: *a-b*
	Mg. per gram					
H_2O	0.45	0.40	0.29	0.16	0.11	0.05
NaCl, 3%	0.49	0.43	0.46	0.03	..	0.06
Tartaric acid, 1%	0.48	0.40	0.44	0.04	..	0.08
HCl, 1%	0.37	0.35	0.32	0.05	0.03	0.02
Untreated	0.48	0.44	0.32	0.16	0.12	0.04

Table XVII. Effect of Temperature and Time of Blanching on Ascorbic Acid Oxidase (Series II)

Temp. ° *C.*	Time *Min.*	Ascorbic Acid Present: Unheated control, *a*	Ascorbic Acid Present: Heated control, *b*	Ascorbic Acid Present: Untreated, *c*	Ascorbic Acid Destroyed in 15 Min.: *a-c*	Ascorbic Acid Destroyed in 15 Min.: *b-c*	Ascorbic Acid Destroyed in 15 Min.: *a-b*
No treatment		0.54	0.48	0.14	0.40	0.34	0.06
71.1	5	0.60	0.52	0.54	0.06	..	0.08
76.6	5	0.60	0.53	0.56	0.04	..	0.07
82.2	3	0.61	0.52	0.55	0.06	..	0.09
87.8	3	0.62	0.53	0.57	0.05	..	0.09
100	1	0.55	0.48	0.50	0.05	..	0.07
100	2	0.53	0.47	0.51	0.02	..	0.06

Table XVIII. Effect of Acetaldehyde and Catalase Contents on Quality of Stringbeans

Temp. ° *C.*	Blanching Time *Min.*	Color	Texture	Remarks	Catalase Factor	Acetaldehyde *P. p. m.*
			Series I			
20	2	Brown	Tough	Off-flavor	0.111	25.0
40	2	Brown	Tough	Off-flavor	0.115	24.2
65	2	Olive green	Tough	Off-flavor	0.033	9.6
77.5	2	Olive green	Tough	Off-flavor	0.0000	8.8
80	2	Olive green	Tough	Off-flavor	....	5.2
82.5	2	Olive green	Tough	Fair flavor	....	...
85	2	Good	Firm	Fair flavor	....	...
87.5	2	Good	Firm	Fair flavor	....	4.8
90	2	Good	Mushy	Fair flavor	....	...
100	2	Good	Very mushy	Poor flavor	....	3.5
			Series II			
71.1	5	Good	Tough	Off-flavor	0.0087	11.0
76.7	5	Good	Tough	Off-flavor	0.0000	8.36
82.2	3	Good	Firm	Very slight off-flavor	....	11.88
82.2	5	Good	Firm	Good flavor	....	3.96
87.8	3	Good	Mushy	Good flavor	....	...
87.8	5	Good	Mushy	Good flavor	....	...
93.3	3	Good	Mushy	Good flavor	....	...
93.3	5	Good	Mushy	Good flavor	....	4.86
100	1	Olive green	Firm	Slight off-flavor	0.0045	3.96
	2	Good	Firm	Good flavor	0.0000	3.96
	3	Good	Mushy	Fair flavor	....	...
	4	Good	Mushy	Fair flavor	....	...
	5	Good	Mushy	Fair flavor	....	2.20

under various conditions were studied in relation to flavor retention during storage at −17° C. It was found that acetaldehyde, a known product of anaerobic respiration, accumulates in samples containing active catalase. The amount of acetaldehyde is smaller, the lower the catalase activity, but although it decreases regularly with decrease in the latter, there is no definite relation between the two such as was found for peas (*1*). The catalase activity and acetaldehyde content decrease as the quality of the product improves (Table XVIII) but they are not a reliable index of flavor retention. The rate of heat inactivation of catalase is definitely more rapid than that of the agencies producing off-flavors. The ascorbic acid oxidase activity closely parallels that of catalase and is reduced by heating at about the same rate. The peroxidase activity as measured by the rate of decomposition of hydrogen peroxide in the presence of pyrogallol is definitely more resistant to heat inactivation than catalase. On comparing the temperature and time necessary for its destruction with those required for retention of flavor, we find that there is a fairly close correlation between its inactivation and keeping quality. Thus, in stringbeans, peroxidase activity would probably serve as a better index of quality than would catalase activity.

However, it is difficult from the quantitative data obtained by the method used to determine just how much of the peroxidase present must be destroyed for flavor retention. Apparently it need not be all destroyed. The usual qualitative tests showed that the benzidine peroxidase of beans was surprisingly thermostable, while the guaiacum peroxidase was inactivated in samples that were found quantitatively to be low in peroxidase. Apparently the peroxidase system of stringbeans is quite complex. There was a fair correlation between the heating conditions necessary for flavor retention and those required to inactivate the guaiacum peroxidase. A very thermolabile oxidase was observed to be present in stringbeans.

Impregnation with hydrochloric acid inactivated catalase, peroxidase, and ascorbase activity. Impregnation with sodium chloride and tartaric acid decreased catalase activity and inactivated ascorbase but did not noticeably effect peroxidase activity; however, the vegetables impregnated with hydrochloric and with tartaric acid were so badly disintegrated by these agents that they were not fit for use.

The enzyme activity in immature uncut beans was greater than that of the cut mature beans. Thus it is necessary, as is also shown by organoleptic tests, that maturity be taken into consideration when blanching. In series II, uncut stringbeans were used and a longer blanching period was thus required to obtain the necessary heat penetration.

A satisfactory product was obtained by blanching cut stringbeans for 2 minutes at 85° to 87.5° C., for 5 minutes at 82.2° C., and for 2 minutes at 100° C. in less mature uncut stringbeans.

Literature Cited

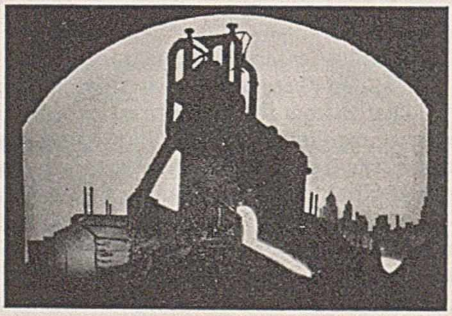
(1) Arighi, A. L., Joslyn, M. A., and Marsh, G. L., Ind. Eng. Chem., 28, 595 (1936).

(2) Bitting, A. W., "Appertizing. The Art of Canning, Its History and Development", p. 395, San Francisco, Trade Pressroom, 1937.

(3) Joslyn, M. A., *Quick Frozen Foods*, 1 (2), 10–13 (1938).

(4) Joslyn, M. A., Bedford, C. L., and Marsh, G. L., Ind. Eng. Chem., 30, 1068 (1938).

(5) Joslyn, M. A., and Marsh, G. L., *Food Industries*, 10, 379, 435 (1938); *Western Canner and Packer*, 30, No. 5, 21; No. 7, 35; No. 8, 20 (1938).



Preparation of Pure Cyclohexane

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THE best cyclohexane available through most of the leading chemical dealers has a freezing point between 3.5° and 4.5° C. Timmermans (*13*) and others have shown that the freezing point of the pure substance lies close to 6.4° C. Since the physicochemical properties of the hydrocarbon make it a useful solvent for many purposes, a simple method of purification seemed highly desirable.

The impurities may arise from two sources: (*a*) side reactions during hydrogenation and (*b*) the nature of the benzene utilized. Although Sabatier (*9*) claimed that no side reactions took place when nickel was used as a catalyst, others found that this was not invariably true. Thus Burrows and Lucarini (*1*), studying the equilibrium of benzene, hydrogen, and cyclohexane, had to discontinue the use of nickel because of side reactions; they substituted platinum instead. The side reaction which is most likely to occur is the scission of the benzene ring with the formation of methylcyclopentane. Recently, Flynn (*4*), working in these laboratories, obtained information as to the extent of these side reactions by hydrogenating benzene over a nickel catalyst at 170° C. By recycling the condensate over the nickel in an atmosphere of hydrogen, he obtained a completely saturated liquid whose freezing point was approximately −40° C. after the benzene had been removed by treatment with sulfuric and nitric acids. This C. P. benzene had previously been purified by three recrystallizations in order to remove traces of the xylenes and toluenes which are ordinarily present. Calculations based on the latent heats of fusion of cyclohexane and methylcyclopentane would indicate that a mixture of the two, with a freezing point of −40°, should have a composition of about 30 per cent methylcyclopentane.

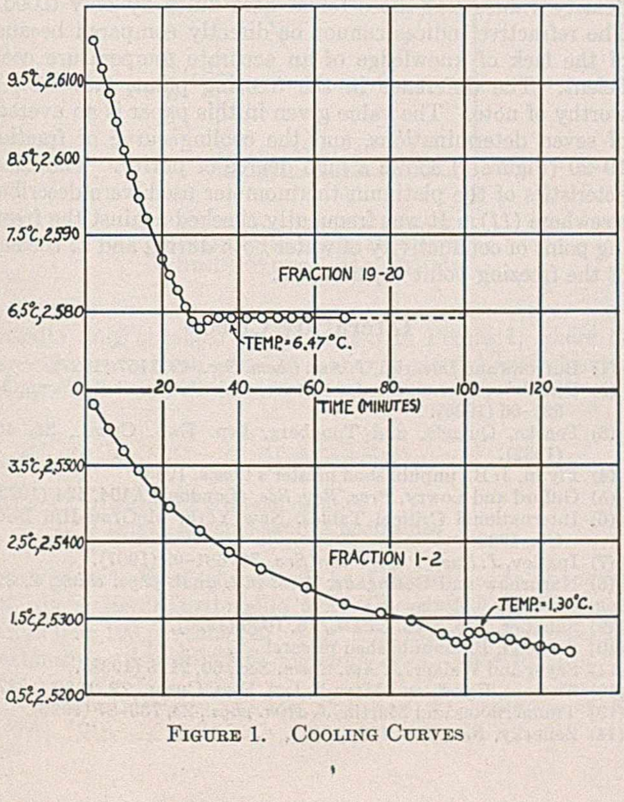

FIGURE 1. COOLING CURVES

Thermodynamic calculations indicate that methylcyclopentane will be even more likely to form than cyclohexane. Thus from the data and method given by Thomas, Egloff, and Morrell (*12*), the free energy change for the reaction,

$$C_6H_6 + 3H_2 \longrightarrow C_5H_{11}.CH_3 \qquad (1)$$

is $\Delta F°_{441} = -19{,}762$; and for the reaction,

$$C_6H_6 + 3H_2 \rightarrow C_6H_{12} \qquad (2)$$

the free energy change is $\Delta F°_{441} = -4534$. It is possible that the method of making the catalyst may influence the course of reaction, for Ipatiev (*7*) claimed to have produced only cyclohexane when nickel sesquioxide was used.

Evidence is presented to show that methylcyclopentane is likely to be produced in the hydrogenation of benzene with a nickel catalyst. Pure cyclohexane can be produced from the commercial material by rectification in a Fenske, Quiggle, and Tongberg column.

Extensive recrystallizations of the best cyclohexane obtainable from Eastman Kodak Company and the British Drug House, as carried out both by Selwood (*10*) and Flynn (*4*), showed little promise that cyclohexane could be purified this way. Hence rectification in an efficient column seemed to be the only alternative method of preparing this substance in a pure state.

Separation of Fractions

A rectification column was built according to the plans given by Fenske, Quiggle, and Tongberg (*3*). The dimensions, however, were altered to suit the space available. The column proper was made of a copper pipe 2.54 cm. o. d. and 4 meters long. It was filled with a No. 18 jack chain. The still was a copper-plated iron pot, insulated and bound with Nichrome wire so that it could be heated both from the sides and bottom.

A reflux ratio of about 35 to 1 was maintained by keeping the temperature difference between the still and condenser head constant at 11.5° C. The product was withdrawn in 100-cc. fractions every 2 hours. In this manner over 3000 cc. of the Eastman Kodak Company's commercial cyclohexane were separated into thirty fractions. They were then examined for purity by density, refractive index, and freezing point measurements.

DENSITY. The densities were measured with a hydrometer, graduated to four decimal places. It was calibrated by immersing it in two samples of cyclohexane whose densities had been carefully determined previously by means of a standard 50-cc. specific gravity bottle. All measurements

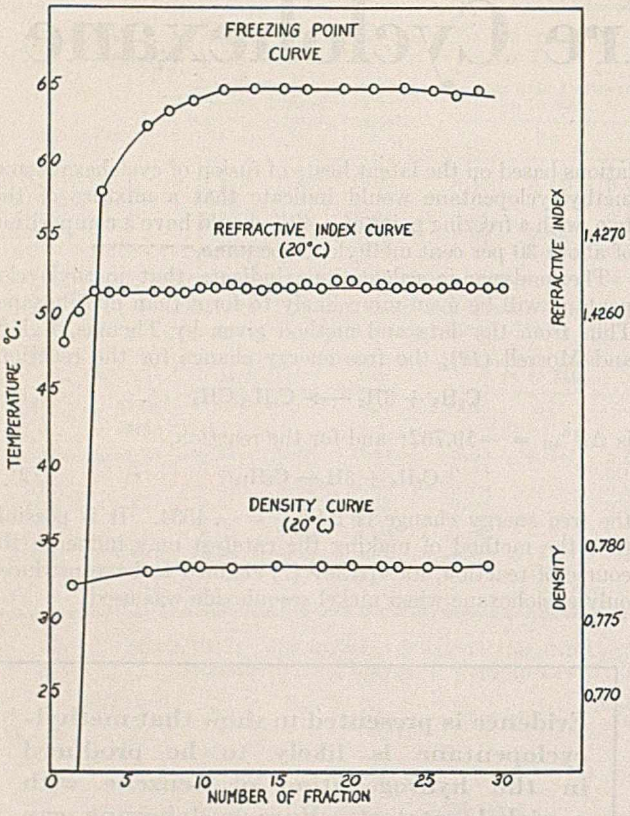

Figure 2. Physical Properties of Fractions

were carried out at 20° C. in a constant-temperature bath whose variation was not greater than 0.03° C. The mercury thermometer had been calibrated against a platinum resistance thermometer recently checked by the Bureau of Standards for accuracy.

Refractive Index. The refractive indices were measured by a Pulfrich refractometer constructed by Adam Hilger. Powdered sodium chloride sprayed into a Bunsen burner flame served as a source of monochromatic light. Water at 20° C. from the constant-temperature bath was led through the apparatus at such a rate that no difference in temperature reading could be detected between the bath and the refractometer cup.

Purity of the Fractions

Freezing Point. The apparatus used was described by Seyer and Walker (*11*). The bath fluid was water and ice, and was kept stirred by a small motor. The cyclohexane was stirred by hand once every 5 seconds to obtain constant results, because the heat of fusion of this hydrocarbon is so low. For freezing point determinations two of the 100-cc. fractions were combined in order to have sufficient liquid in the freezing point chamber.

To show the difference in behavior of the various fractions, the cooling curves of fractions 1–2 and 19–20 are given in Figure 1. The densities (corrected to vacuum), refractive indices, and freezing points of the fractions are listed in Table I.

The results are shown graphically in Figure 2. Since the freezing point is the most sensitive to impurities of the physical properties measured, it is obvious that fractions 11 to 26, inclusive, constitute pure samples of cyclohexane. In other words, a yield of 50 per cent of pure cyclohexane can be obtained from the commercial variety by using a column such as has been described. A rerun of most of the fractions would certainly increase the yield.

Table I. Physical Properties of Fractions

No. of Fraction	d_4^{20}	n_D^{20}	Freezing Point, ° C.	No. of Fraction	d_4^{20}	n_D^{20}	Freezing Point, ° C.
1	0.7771	1.42562	..	16	....	1.42632	6.47
2	....	1.42606	1.30	17	....	1.42637	..
3	0.7775	1.42627	..	18	0.7784	1.42632	6.46
4	....	1.42627	5.79	19	....	1.42642	..
5	....	1.42627	..	20	0.7784	1.42642	6.47
6	0.7780	.....	..	21	0.7784	1.42632	..
7	....	1.42627	6.23	22	0.7784	1.42637	6.48
8	....	1.42627	6.32	23	0.7784	1.42637	..
9	0.7784	1.42627	..	24	....	1.42632	6.48
10	0.7784	1.42632	6.40	25	0.7784	1.42632	..
11	....	1.42632	..	26	....	1.42632	6.46
12	0.7784	1.42637	6.47	27	0.7784	1.42632	6.44
13	....	1.42632	..	28	....	1.42632	..
14	....	1.42627	6.48	29	0.7784	.....	6.46
15	0.7784	1.42632	..	30	....	1.42632	..

The average values of the densities, refractive indices, and freezing points of the pure samples are, respectively, 0.7784, 1.42635, and 6.47 ± 0.02° C. These results agree well with those given by other investigators and summarized in Table II.

Table II. Comparison of Results with Those of Other Investigators

	Density	Refractive Index	Freezing Point, ° C.
Timmermans and Martin (*13*)	0.7785 (20° C.)	1.42886 (15° C.)	6.40
Zelinsky (*14*)	0.7788 (19.5° C.)	1.4289 (19.5° C.)	6.40
Gifford and Lowry (*5*)	...	1.42900 (15° C.)	6.28
Intern. Critical Tables (*6*)	...	...	6.50
Burrows and Lucarini (*1*)	...	1.42640 (20° C.)	..
Nagornow and Rotinganz (*8*)	0.7786 (20° C.)	...	6.54
Eisenlohr (*2*)	0.7783 (20° C.)	...	..
Present values	0.7784 (20° C.)	1.42635 (20° C.)	6.47

The tables show that the present values fall well within those given by others. Considerable weight must be given the values of Timmermans and Martin (*13*), who were very careful to prepare a pure compound. The difference in their density values and those found here differ by only 0.0001. The refractive indices cannot be directly compared because of the lack of knowledge of an accurate temperature coefficient. The difference in the freezing point, 0.07° C., is worthy of note. The value given in this paper is an average of seven determinations, and the cooling curve of fraction 19–20 (Figure 1) shows a high degree of purity. The characteristics of the platinum thermometer used were described elsewhere (*11*). It was frequently checked against the freezing point of conductivity of water both during and at the end of the freezing point experiments.

Literature Cited

(1) Burrows and Lucarini, *J. Am. Chem. Soc.*, 49, 1157 (1927).
(2) Eisenlohr, *Fortschritte der Chemie, Physik, physikal. Chem.*, 18, 521–66 (1925).
(3) Fenske, Quiggle, and Tongberg, Ind. Eng. Chem., 24, 408 (1932).
(4) Flynn, J. B., unpublished master's thesis, 1933.
(5) Gifford and Lowry, *Proc. Roy. Soc.* (London), A104, 434 (1923).
(6) International Critical Tables, New York, McGraw-Hill Book Co., 1926.
(7) Ipatiev, *J. Russ. Phys. Chem. Soc.*, 39, 681–93 (1907).
(8) Nagornow and Rotinganz, *Ann. inst. anal. phys. chim.*, 2, 371 (1924).
(9) Sabatier, Ind. Eng. Chem., 18, 1006 (1926).
(10) Selwood, P., unpublished research.
(11) Seyer and Walker, *J. Am. Chem. Soc.*, 60, 2125 (1938).
(12) Thomas, Egloff, and Morrell, Ind. Eng. Chem., 29, 1260 (1937).
(13) Timmermans and Martin, *J. chim. phys.*, 23, 733–87 (1926).
(14) Zelinsky, *Ber.*, 39, 2799 (1901).

Specific Heat of Strained Rubber

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The specific heat of two samples of rubber and its variation with extension were determined. One of the samples was highly vulcanized, the other unvulcanized. The measurements were made at room temperature (19° to 21° C.) and involved temperature changes of less than 0.1° C.

The specific heat of neither sample varied much with extension. This result is not in agreement with previous data which indicated a decrease in specific heat of about 30 per cent at 100 per cent extension.

THE specific heat of unstrained rubber as a function of temperature has been the subject of many investigations; but only one set of data has been published on the specific heat of strained rubber.[1] Ornstein and his co-workers heated samples of strained vulcanized rubber to 80° C. and dropped them into a calorimeter at room temperature. The results they obtained are presented in Figure 1, where the specific heat of one gram of rubber is plotted against extension:

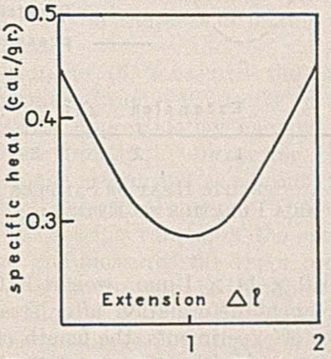

FIGURE 1. SPECIFIC HEAT OF STRAINED RUBBER, AFTER ORNSTEIN, WOUDA, AND EYMERS

$$\Delta l = \frac{l - l_0}{l_0}$$

where l = length of strained sample
l_0 = length of same sample unstrained

As Figure 1 shows, the specific heat diminishes to about two thirds of its original value when the extension is increased from 0 to 100 per cent ($\Delta l = 1$); it increases again on further extension. According to Ornstein *et al.*, "the form of the curve for the specific heat is most interesting, as the strong variation of this quantity with the elongation must be of utmost importance for the understanding of the molecular state of rubber."

In order to check these results by another method, the writer measured the specific heat of rubber at room temperature (19° to 21° C.) by a process involving temperature changes of less than 0.1° C. Two samples of rubber were chosen. Sample I was highly vulcanized for 30 minutes under 3 atmospheres pressure. Its composition was as follows:

Smoked sheet	89
Sulfur	1.8
Accelerator	0.9
ZnO, carbon black	8.3

Sample II was a patented, pure crepe, milled, pressed, calendered rubber; it was unvulcanized and contained no fillers. A band-shaped piece of rubber was cut from each sample, the same piece was studied at several extensions.

Calorimeter

The heating unit (Figure 2) is made of constantan wire, 0.2 mm. in diameter, with a resistance of 7.6 ohms; it is coiled around the thin-walled copper tube, *A* (10 mm. in diameter, 75 mm. long, 0.1 mm. thick) and insulated with Bakelite. One end of the band-shaped rubber, *B*, is held by a steel pin, *C*, soldered transversely through the copper tube. The rubber is then wound over the heating unit under a constant strain produced by a weight attached to the free end. The latter is finally attached also to the same pin. One of the copper-constantan junctions of the thermocouple (constantan 0.2 mm., copper 0.15 mm.) is thus placed between the heating unit and the rubber band; the other junction, *D*, is forced into a hole in the center of a 70-gram copper block. The calorimeter is placed in a glass container with a ground joint and can be evacuated. The rubber and the internal face of the glass container are covered by light aluminum foils, *E*, which reduce the losses by radiation. The whole apparatus is immersed in a Dewar flask.

The thermocouple is connected to a Kipp and Zonen galvanometer, type Zc. The heating coil and its connections (which serve also to suspend the heating unit) are not shown in Figure 2.

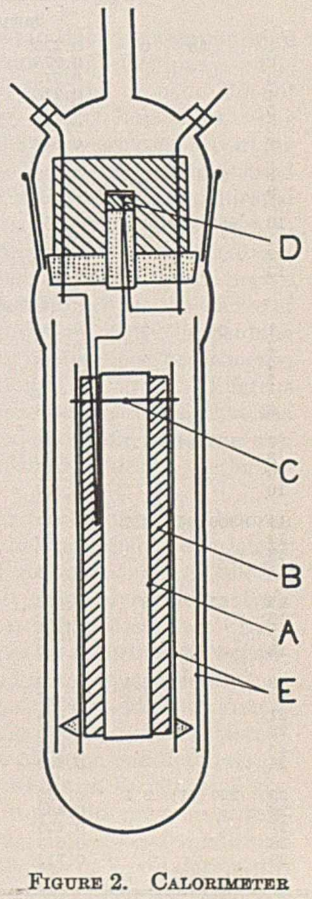

FIGURE 2. CALORIMETER

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[1] Ornstein, Wouda, and Eymers, *Proc. Acad. Sci. Amsterdam*, **33**, 273 (1930).

Calibration and Measurements

The two junctions of the thermocouple are attached to the bulbs of two Beckmann thermometers and placed in two Dewar flasks filled with water of slightly different temperatures. During temperature equalization, readings of the arbitrary temperatures indicated by the two thermometers and of the position of the spot on the galvanometer scale are made every 2 minutes. The difference between the readings of the two thermometers is plotted against those of the galvanometer (Figure 3). The slope of the curve thus obtained gives the calibration. In the present case a 100-mm. displacement of the spot corresponds to a temperature difference of 0.092° C. with an accuracy better than one per cent.

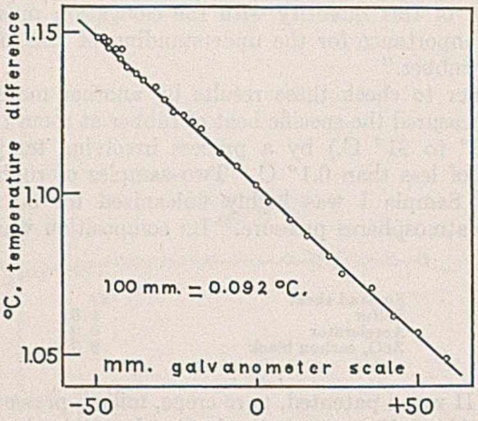

FIGURE 3. CALIBRATION OF THE GALVANOMETER

TABLE I. SUMMARY OF DATA

Expt. No.	Cm.	Δl	Energy Input Calories	Temp. Increase ° C.	Total Heat Capacity Cal./° C.	Specific Heat Cal./° C./gram	Av. Specific Heat
				Sample I			
1	58	0	0.275	0.0049	5.65	0.375	
2			0.275	0.0049	5.65	0.375	
3			0.275	0.0048	5.75	0.38	
4			0.275	0.0050	5.54	0.365	
5			0.426	0.0072	5.95	0.40	
6			0.426	0.0075	5.72	0.38	
7			0.873	0.0151	5.78	0.385	0.38
8	96 (58)	0.65	0.393	0.0069	5.70	0.38	
9			0.565	0.0098	5.80	0.385	0.385
10	166 (58)	1.9	0.56	0.0102	5.50	0.365	
11			0.56	0.0100	5.58	0.37	
12			0.273	0.049	5.62	0.37	
13			0.79	0.0140	5.65	0.375	0.37
				Sample II			
1	64	0	0.285	0.0058	4.92	0.395	
2			0.287	0.0061	4.73	0.375	
3			0.448	0.0100	4.47	0.35	
4			0.670	0.0140	4.78	0.38	
5			0.407	0.0083	4.92	0.395	
6			0.573	0.0119	4.83	0.385	0.38
7	170 (64)	1.7	0.573	0.0109	5.27	0.43	
8			0.330	0.0063	5.28	0.43	
9			0.560	0.0109	5.16	0.42	
10			0.447	0.0086	5.22	0.425	0.43
11	300 (64)	3.7	0.447	0.0083	5.40	0.445	
12			0.289	0.0054	5.33	0.435	
13			0.440	0.0082	5.37	0.44	
14			0.534	0.0100	5.37	0.44	0.44
15	67	0	0.673	0.0135	4.97	0.40	
16			0.420	0.0081	5.18	0.42	
17			0.482	0.0097	4.99	0.40	
18			0.206	0.0041	5.18	0.42	0.41
19	105 (69)	0.5	0.527	0.0106	4.98	0.40	
20			0.407	0.0079	5.13	0.415	
21			0.374	0.0075	4.98	0.40	
22			0.475	0.0100	4.78	0.38	
23			0.622	0.0128	4.86	0.39	
24			0.289	0.0057	5.07	0.41	0.40
25	220 (71)	2.1	0.425	0.0083	5.13	0.415	
26			0.462	0.0089	5.17	0.42	
27			0.425	0.0084	5.08	0.41	
28			0.613	0.0117	5.25	0.43	
29			0.712	0.0141	5.07	0.41	0.42

One hour after the rubber band is mounted, readings of the galvanometer are made at intervals of 30 seconds over a period of several minutes. A current of known intensity (between 0.08 and 0.18 ampere) is sent through the heating coil for 5 to 30 seconds, and the readings are continued for 5 minutes. (It was found that a regular slope of the time-deflection curve is practically attained after 2 minutes.) The increase of temperature corresponding to a known energy input and thus the total heat capacity of the rubber and the heating unit can be easily deduced. The heat capacity of the heating unit, calculated from its components (copper, constantan, aluminum, Bakelite), was found to be 0.97 calorie per ° C., about 20 per cent of the heat capacity of the rubber band. By deducting 0.97 from the total heat capacity and dividing by the weight of the rubber, we obtain the specific heat of the rubber.

Results

The experimental data are given in Table I and summarized in Figure 4, where the values of Ornstein are reproduced for comparison.

SAMPLE I (580 × 11 × 2 mm., weight 12.5 grams) shows practically no permanent deformation after straining. The specific heat does not change with extension between 0 and 1.9.

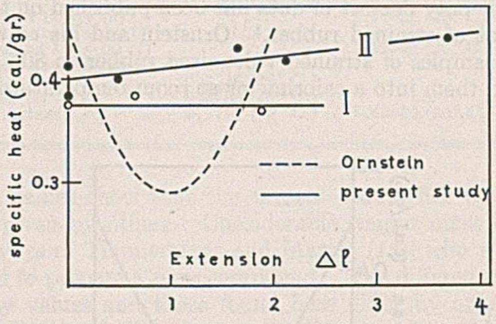

FIGURE 4. SPECIFIC HEAT OF SAMPLES I AND II AS A FUNCTION OF EXTENSION

SAMPLE II (640 × 14 × 1 mm., weight 10.0 grams) shows a marked permanent deformation after straining. At the end of the series of experiments, the length of the band was 710 mm., as compared with 640 mm. at the beginning. To give consideration to the possible influence of this change on the specific heat, extensions were tried in the following order: 0, 1.7, 3.7, 0, 0.5, 2.1. The interpolation in Figure 4 seems to indicate a slow increase of the specific heat with the extension, but this increase is near the limits of reproducibility.

The results obtained with both samples do not confirm the large decrease in specific heat with extension, found by Ornstein. Ornstein and his co-workers measured a "mean specific heat" over a temperature interval of 60° C. The transformations which may occur in strained rubber when it is heated to 80° C. and then suddenly cooled may be accompanied by considerable evolution of heat.

Phase Equilibria in Hydrocarbon Systems

Latent Heat of Vaporization of Propane and *n*-Pentane[1]

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AND W. N. LACEY
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The latent heat of vaporization was measured experimentally for propane at temperatures from 100° to 170° F. and for *n*-pentane from 80° to 200° F. The apparatus employed for these measurements is described in detail. The results are presented in both tabular and graphical form. A comparison is made between the results obtained and the data of other investigators.

THE latent heat of vaporization is of importance in establishing the thermodynamic behavior of pure substances in the two-phase region. Although this quantity may be calculated from volumetric and vapor pressure data by means of the Clapeyron equation, it can be measured direct in certain regions more accurately. This measurement also affords a desirable check upon the consistency of thermodynamic data related to the saturated liquid and gas. For this reason an experimental investigation was made of the latent heat of vaporization of propane and *n*-pentane at temperatures from 80° to as high as 200° F. This work is part of a general study of the heat of mixing of the lighter paraffin hydrocarbons.

Dana and co-workers (*2*) measured the latent heat of vaporization of propane from −40° to 68° F. with an estimated uncertainty of approximately one per cent. These data were obtained directly by measuring the weight of propane evolved from a calorimeter as a result of the addition of a known quantity of electrical energy. These investigators also determined the specific volume of the saturated liquid and saturated gas, and measured the vapor pressure of propane throughout the above-mentioned temperature interval. They compared values of the latent heat of vaporization calculated from these volumetric and pressure data with the directly measured values.

Pressure-volume-temperature measurements from the authors' laboratory (*13*) also permitted the calculation of the latent heat of vaporization of propane by the use of the Clapeyron equation. These data indicated values approximately 6 B. t. u. per pound lower than values obtained by Dana and co-workers (*2*) by extrapolation of their measurements at lower temperatures. This large discrepancy caused doubt as to the proper value of the latent heats of vaporization for propane at temperatures below 160° F.

The heat of vaporization of commercial *n*-pentane at temperatures between −4° and 86° F. was measured by Griffiths and Awbery (*3*) who expressed their results as a linear function of the temperature. They also reported data upon the specific volumes of saturated gaseous *n*-pentane at temperatures from 32° to 88° F. The specific volumes of the saturated liquid and the saturated gas of *n*-pentane as well as the vapor pressure were measured by Young (*15*) at temperatures from 70° to the critical temperature (387° F.). The measured values of Griffiths and Awbery (*3*) are in only fair agreement with values calculated from the pressure-volume-temperature measurements reported by Young. The vapor pressure and the volumetric behavior of liquid *n*-pentane were studied in the authors' laboratory at temperatures between 70° and 220° F. (*12*). These data were in good agreement with the measurements made by Young.

Materials and Method

The propane and *n*-pentane used in this investigation were obtained from the Phillips Petroleum Company. The special analyses furnished showed that the propane did not contain more than 0.03 mole per cent of impurities. The sample of *n*-pentane contained 99.3 mole per cent *n*-pentane and 0.7 mole per cent isopentane. The propane was used without further purification, but the *n*-pentane was subjected to a fractionation in a column packed with glass rings in order to remove dissolved air and some of the isopentane. The purity of these samples was substantiated by the degree of constancy of their vapor pressure throughout the course of isothermal condensation. The presence of the isopentane in the sample of *n*-pentane was not of serious consequence since its latent heat of vaporization is not greatly different from that of *n*-pentane. It is believed, therefore, that the presence of the impurities indicated above did not cause any appreciable uncertainty in the reported values of the latent heat of vaporization.

The method employed is similar to that used by Osborne and co-workers (*5*, *6*, *7*) in their investigation of the latent heat of vaporization of water and ammonia. Since Osborne (*5*) has already made an excellent thermodynamic analysis of the behavior of such a device, it is unnecessary to derive the expressions that were employed in reducing the experimental data to the desired thermodynamic quantities.

In principle, the method consisted of adding a known amount of electrical energy to a calorimeter containing liquid and gas phases of the substance in question and determining the weight of material that was withdrawn as saturated gas in order to maintain the temperature and pressure within the calorimeter at constant values. Under ideal conditions in which there is no superheat of the gas or liquid during the isothermal evaporation process, the latent heat of vaporiza-

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[1] This is the twenty-fourth paper in this series. Previous articles appeared during 1934 to 1938, inclusive, and in March, 1939.

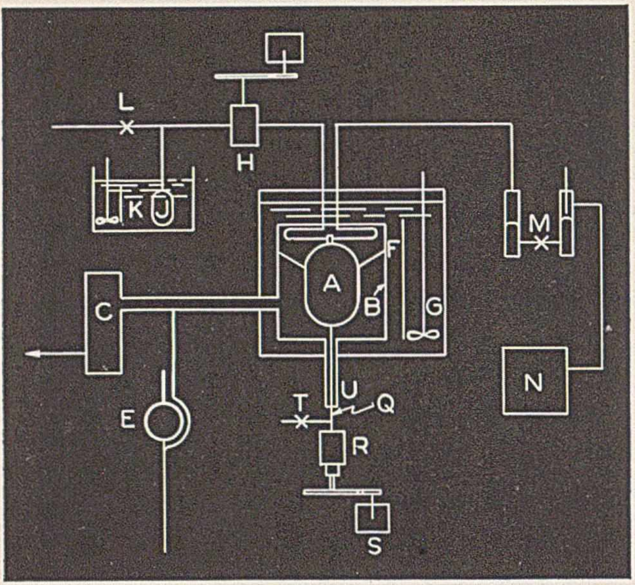

FIGURE 1. DIAGRAM OF APPARATUS

tion is simply related to the electrical energy added by means of the following expression:

$$L = \frac{Q_e - Q}{\Delta m}\left(\frac{V_d - V_b}{V_d}\right) \qquad (1)$$

However, additional correction terms are required when the actual process digresses from the above-mentioned ideal vaporization process. In the present instance the maximum total of all of the corrections amounted to only 0.6 per cent of the latent heat of vaporization. These corrections were applied in a manner similar to that proposed by Osborne (*5*). Information concerning the specific heat of the saturated liquid and saturated gas as well as data upon the specific volume and isothermal enthalpy-pressure coefficient $(\partial H/\partial P)_T$ of both of the phases is required in the evaluation of these corrections. In addition, the heat capacity of the empty calorimeter must be known in order to determine the net energy added to the system when digressions from an isothermal vaporization process are encountered.

Apparatus

The apparatus developed for making the measurements reported in this paper is depicted in Figure 1:

The calorimeter bomb, *A*, was mounted within the vacuum jacket, *B*. The space between the calorimeter and the jacket was maintained at a pressure below 10^{-7} inch of mercury by means of the oil diffusion pump, *C*. This pressure was measured by means of the McLeod gage, *E*. It was found that the quantity of condensable vapor within the vacuum space was sufficiently small so that the pressure measurements by means of the McLeod gage gave a satisfactory indication of the resistance to heat transfer by conduction through the space from the bomb to the jacket.

The temperature of the jacket was maintained at the desired value by means of the small oil bath, *F*, of low heat capacity, which was agitated by means of stirrer *G*. A four-junction thermocouple was mounted with one set of junctions on the exterior surface of calorimeter bomb *A* and the other on the interior surface of vacuum jacket *B*. This double-wire copper-constantan (No. 40 B. and S. gage) thermocouple was employed to measure the temperature difference between the bomb and jacket during the course of a given set of measurements. A similar two-junction thermocouple was mounted on the surface of the bomb and the interior of the jacket. This latter thermocouple was connected to a high-sensitivity low-resistance galvanometer. The light beam from this galvanometer actuated a photoelectric relay which in turn controlled the electrical energy added to the jacket bath. This arrangement was used when the heat capacity of the calorimeter was being evaluated and permitted the automatic maintenance of a temperature difference of nearly zero between the interior surface of the jacket and the exterior of the calorimeter bomb. In general, temperature differences of not more than 0.02° F. were encountered in the course of a particular set of measurements of this type. For the actual measurements of latent heat of vaporization, the temperature of the jacket oil bath was controlled at a constant value by means of a four-junction thermocouple operating between an ice bath and the thermostat. This four-junction thermocouple in conjunction with a potentiometer actuated the high-sensitivity galvanometer which controlled the same photoelectric relay mentioned in connection with the differential control apparatus. This control device maintained the temperature of the vacuum jacket within 0.01° F. of the desired value. Oil bath *F* was placed within an air thermostat which was maintained at a temperature approximately 2° F. below that of the calorimeter.

Calorimeter bomb *A* was connected to the motor-operated valve, *H*, by means of a small stainless-steel tube approximately 0.02 inch in inner diameter. This tube was in good thermal contact with the jacket, avoiding any thermal gradient in this tube adjacent to the calorimeter bomb. All of the tube outside of oil thermostat bath *F* was enclosed in an isobaric steam jacket to avoid any condensation in this part of the apparatus. The work of Osborne and co-workers emphasized (*6*) the importance of avoiding such condensation. The weighing bomb, *J*, was immersed in the condenser thermostat bath, *K*, which was maintained at a predetermined temperature, lower than that of the calorimeter bomb. This temperature was so chosen that a pressure differential of approximately 4 pounds per square inch was maintained across the motor-operated valve, *H*, which was remotely controlled from the location of the temperature measuring equipment. The calorimeter could be evacuated through valve *L*. The pressure existing within the calorimeter was measured by means of a pressure balance, *N*, which was connected to it through the oil-mercury interface in the U-tube, *M*. The exterior of tube *M*, as well as that of the tubing connecting it with the calorimeter bomb, was steam-heated to avoid condensation.

The details of the construction of the calorimeter bomb are presented in Figure 2:

The bomb was machined from solid bar stock which, after heat treatment, exhibited an elastic limit in excess of 200,000 pounds per square inch. The hemispherical ends were threaded to the cylindrical section and were soldered to it with block tin. Adequate agitation of the contents of the calorimeter was desirable in order to avoid undue superheating of the liquid and inequalities in the temperature within the calorimeter. This was accomplished by placing a small centrifugal agitator, *Y*, within the calorimeter bomb, similar in some respects to that employed by Osborne and Van Dusen (*7*). This agitator circulated the liquid upward around shield *W* past heater *P*. The pump was mounted upon jewel bearings and was driven externally by means of a small (0.01-inch) piano wire which was enclosed in the stainless-steel tube, *Q*. Outside the vacuum jacket this piano wire passed through the packing gland, *R*, of Figure 1 and was driven by means of the electric motor, *S*. A valve, *T*, was provided above the packing gland to permit the addition and withdrawal of samples of liquid from the calorimeter. The apparatus was so designed that less than 0.03 cubic inch (0.4 cc.) of free space existed in stainless steel tube *Q* and packing gland *R*. This quantity was small in comparison with the volume of the calorimeter which was approximately 18.3 cubic inches (300 cc.).

Heater *P* of Figure 2 was constructed of approximately 3 feet of No. 36 constantan wire enclosed within a small (0.03-inch inner diameter) stainless-steel tube. It was so constructed that all of the constantan wire was within the calorimeter bomb and only relatively large (No. 28 B. and S. gage) copper leads were brought out of the calorimeter. The voltage impressed upon the heater was measured by means of potential leads connected to the heater at the exterior surface of the calorimeter bomb. Since this electromotive force was approximately 9 volts, a volt box with a resistance of 10^4 ohms was employed in conjunction with a recently calibrated Leeds & Northrup type K-2 potentiometer for its measurement. Intercomparisons of the various unsaturated cadmium standard cells employed in the laboratory indicated that this voltage was measured with an uncertainty of not more than one part in ten thousand. The current flowing through the heater was established by measuring the potential across a standard resistance connected in series with heater *P*. It is believed that the current flowing was measured with an uncertainty of not more than two parts in ten thousand. Each of these quantities (i. e., the current and the voltage) was corrected for the flow of current through the volt box and for the resistance of the heater leads from the potential connections to the heater. The time during which the electrical energy was added to the calorimeter was determined by means of an electrical timing device operated by the power supply to the laboratory. It is believed that in the period involved in a given measurement (more than 1000 seconds) no uncertainties greater than 0.05 per cent were involved in this quantity. Storage batteries of adequate capacity were employed as the current source of the calorimeter heater. Changes in the rate of energy addition of more than 0.1 per cent were usually not encountered in the course of a given set of measurements. These batteries were maintained in closed circuit for a period of at least one hour before their use with the calorimeter in order to avoid initial changes in voltage upon closing the circuit. It is believed that the energy added to the heater within the calorimeter was known with an uncertainty of not more than 0.1 per cent.

The temperature of the liquid within the calorimeter was established by means of the single-junction copper-constantan thermocouple, *V*, of Figure 2. This thermocouple was of three-wire construction and was calibrated accurately after its installation within the apparatus against mercury-in-glass thermometers which had been standardized recently at the U. S. Bureau of Standards. The electromotive force measurements for all of the precision thermocouples used in connection with the calorimeter were made by means of a White double potentiometer with which temperature differences as small as 0.005° F. could be detected. The standard cell for this instrument was enclosed in a brass thermostat block which showed a maximum variation of approximately 0.1° F. throughout any particular month. Three standard cells were placed in this thermostat block and were so arranged as to permit their direct intercomparison. Such a comparison indicated a probable uncertainty in standard cell voltage of approximately one part in ten thousand during the entire course of the present investigation. The use of a thermostat container for the standard cells was found to be justified because of the rather large daily fluctuations in the temperature of the laboratory which were found to result in nonequilibrium changes in standard cell voltage of as much as four parts in ten thousand. It is believed that the thermocouples employed permitted the establishment of the temperature of the contents of the apparatus with an uncertainty of not more than 0.1° F. relative to the International Platinum Scale. Changes in temperature in the course of any one measurement of less than 0.001° F. were easily measurable. The temperature of the gas leaving the calorimeter was established by means of a single-junction, three-wire, copper-constantan thermocouple attached to the outlet tube of the calorimeter approximately one inch from the calorimeter bomb. The cold junctions of this thermocouple and of the main thermocouple *V* were immersed in an agitated ice bath.

In order to avoid temperature gradients along the agitator drive tube *Q*, a small manually controlled heater, *U* (Figure 1), was installed. This heater was so controlled that a differential two-junction thermocouple operating between the lower end of this agitator tube and vacuum jacket *B* indicated no measurable temperature difference between these two points. All of the other metallic connections to the calorimeter bomb passed through oil bath *F* and therefore were at substantially the same temperature as the calorimeter bomb.

The material evaporated from the calorimeter was condensed in weighing bombs which had capacities of approximately 2 cubic inches. These bombs were weighed in air with a nearly identical tare, and the change in weight was determined by means of calibrated brass weights. Additions and withdrawals of the contents of the calorimeter by such means indicated that the quantity of material withdrawn could be determined with an uncertainty of not more than 6×10^{-6} pound (3 mg.). Therefore, it is believed that the weight of material evaporated was established with an accuracy of 0.1 per cent for all of the measurements reported in this investigation.

Procedure

The apparatus was first evacuated through valve *L* of Figure 1. A known weight of the hydrocarbon in question was then introduced through valve *T*. A sufficient quantity of material was added so that the liquid level would be approximately 0.75 inch above the top of the circulation shield. The bomb and jacket were then brought to the desired temperature, and the various adjustments made to avoid appreciable thermal leakage from the apparatus. The weighing bomb was attached and immersed in the condenser thermostat bath which was adjusted at the proper temperature relative to the calorimeter. Measurements as a function of time were made of the temperature difference between the jacket and bomb, and of the temperatures of the outlet tube and the interior of the calorimeter bomb. The vacuum jacket was maintained at a constant temperature by the photoelectric control previously described. The agitator was then started and electrical energy added to the calorimeter heater. The motor-operated valve was opened sufficiently to maintain a nearly constant temperature of the contents of the calorimeter. During this evaporative period readings were taken of the temperature difference between the calorimeter bomb and jacket, the temperature of the outgoing gas, and the temperature of the contents of the calorimeter. Each of these quantities was measured at approximately 30-second intervals. During this period measurements of the voltage impressed upon the calorimeter heater and the current flowing through it were also taken at intervals of approximately one minute.

The electrical energy was added for a period of approximately 20 minutes, which corresponded to the removal of from 0.022 to 0.044 pound (10 to 20 grams) of material from the calorimeter. The heater current was then shut off, and readings of the temperature difference and the temperatures were continued until static equilibrium had been reestablished. The motor-operated valve was closed gradually during this period in such a fashion as to maintain a nearly constant bomb temperature. The pressure existing within the bomb was also measured at periodic intervals. However, it was found that the temperature of the evaporating liquid corresponded within small limits (0.05° F.) with the value predicted from the vapor pressure measurements. This indicated that the evaporation from the liquid was taking place substantially at equilibrium. However, approximately 0.2° F. difference in temperature was encountered between the exit gas and the evaporating liquid.

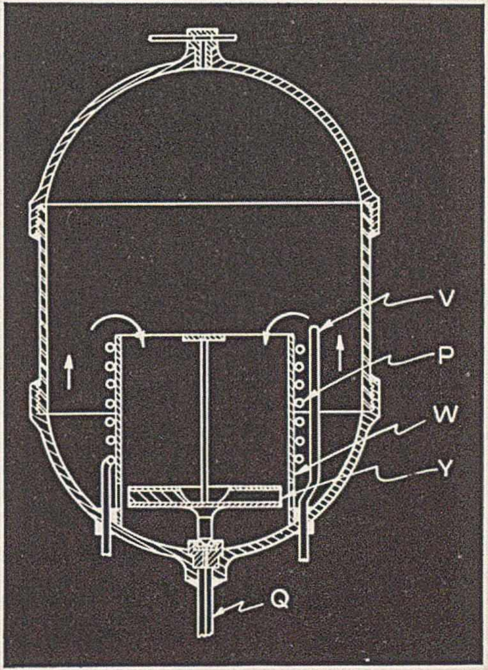

FIGURE 2. CALORIMETER BOMB

The experimental results yielded information concerning the electrical energy furnished to the heater and the weight of material removed from the calorimeter. The temperature of the contents of the calorimeter bomb and of the exit gas, as well as the temperature difference between the calorimeter jacket and the exterior of the bomb, were also available as functions of time. From these data the latent heat of vaporization could be calculated. The isobaric heat capacity and the isothermal enthalpy-pressure coefficient of gaseous propane required in the evaluation of the small correction terms were taken from published data (*10, 14*). Similar data for *n*-pentane were also taken from the literature (*4, 14*). Information concerning the isobaric heat capacity and the isothermal enthalpy-pressure coefficient of liquid propane and *n*-pentane were obtained from earlier investigations (*10, 11, 13, 14*). It is believed that these data are of sufficient accuracy so that they introduce no uncertainties in the resulting values of the latent heat of vaporization greater than 0.03 per cent. Information concerning the specific volume of the saturated liquid and gas is also required in the solution of Equation 1. The specific volume of saturated liquid propane was taken from unpublished direct measurements from the authors' laboratory which are in satisfactory agreement with earlier data (*13*). The specific volume of gaseous propane was based upon some recent direct measurements for superheated propane gas made in the same laboratory, which are in agreement with values reported by Beattie and coworkers (*1*). These data for the superheated gas were used as a basis for determining the specific volume of the saturated gas from the Joule-Thomson coefficients already available (*10*). The specific volume of saturated *n*-pentane liquid was taken from an earlier experimental investigation (*12*). The specific volume of the saturated gas was based upon the data of Rose-Innes and Young (*8*) relating to the specific volume of the superheated gas, in conjunction with available Joule-Thomson measurements (*4*). It is believed that these volumetric data were accurate enough so that no uncertainties greater than 0.2 per cent were introduced by them in the evaluation of the latent heat from the experimental data.

TABLE I. LATENT HEATS OF VAPORIZATION

Temp. ° F.	Latent Heat: Exptl.	Latent Heat: Smoothed	Deviation %	Temp. ° F.	Latent Heat: Exptl.	Latent Heat: Smoothed	Deviation %
	B. t. u./lb.	B. t. u./lb.			B. t. u./lb.	B. t. u./lb.	
			A. Propane				
103.4	132.94	133.98	−0.78	118.4	128.22	126.21	1.59
103.7	133.16	133.84	−0.51	130.7	119.84	119.23	0.51
109.5	130.34	130.92	−0.44	130.9	119.26	119.10	0.13
109.8	132.20	130.76	1.10	144.4	110.21	110.80	−0.53
110.0	132.20	130.66	1.18	144.5	110.67	110.74	0.06
110.1	129.58	130.61	−0.79	162.6	99.56	98.97	0.60
114.4	128.50	128.36	0.11	163.2	99.39	98.17	1.24
118.1	128.07	126.37	1.35	167.0	94.48	95.45	−0.81
			B. *n*-Pentane				
82.3	156.12	155.90	0.14	131.0	147.76	147.44	0.22
103.7	152.58	152.58	0.0	135.1	146.35	146.62	−0.18
104.3	152.69	152.49	0.13	149.0	142.92	143.50	0.40
111.5	151.65	151.24	0.27	154.3	142.63	142.27	0.25
114.4	150.51	150.67	−0.10	158.2	141.21	141.33	−0.09
120.5	149.58	149.55	0.02	180.4	135.65	135.79	−0.10
122.4	148.69	149.18	−0.33	180.5	136.61	135.72	0.66
127.8	148.73	148.11	0.42	200.0	130.38	130.41	−0.02

Results

The latent heat of vaporization of propane was determined at sixteen temperatures between 100° and 170° F. The experimental results are recorded in Table I*A*, together with smoothed values that were obtained by residual interpolation of the experimental data. The deviation of each of the experimental points from these interpolated values has also been included in Table I. The average deviation of the recorded experimental values for propane was 0.77 per cent. All of the experimental results are included, with the exception of a single measurement during which a small leak developed in the weighing bomb. The experimental results were obtained in part with a calorimeter bomb in which there was no internal agitator, but it was impossible to distinguish any systematic variation between the measurements obtained with this equipment and those made with the apparatus described in this paper. The volumetric term indicated in Equation 1 amounts to approximately 20 per cent of the latent heat of vaporization of propane at a temperature of 160° F. This large factor introduces a possible added uncertainty in the data recorded in Table I at the higher temperatures. However, it is believed that no uncertainties larger than 0.2 per cent have been introduced by this term in the calculation of the latent heat of vaporization from the experimental results even at temperatures as high as 167° F.

In general, the direct measurement of the latent heat of vaporization becomes increasingly difficult as the critical state is approached, and it is therefore not surprising that discrepancies somewhat larger than would be indicated by the precision of measurement were encountered in the experimental results. Table II records interpolated values of the latent heat of vaporization at even temperatures throughout the range covered by the experimental investigation. For comparison, the smoothed results published by Dana and co-workers (*2*) are included. The results tabulated are somewhat above the temperature range covered by their investigation, and some added uncertainty probably exists due to this extrapolation. Figure 3 presents the experimental results obtained in this laboratory together with the measurements of Dana *et al.* In the temperature region covered by the experiments of the latter investigators, the curve was drawn through their smoothed points. There is no appreciable inconsistency between the two sets of experimental measurements.

TABLE II. COMPARISON OF LATENT HEAT OF VAPORIZATION RESULTS FOR PROPANE

Temp. ° F.	Exptl., Authors	Exptl., Dana *et al.*[a]	Equation 2, Authors	Temp. ° F.	Exptl., Authors	Equation 2, Authors
	B. t. u./lb.	B. t. u./lb.	B. t. u./lb.		B. t. u./lb.	B. t. u./lb.
60	...	153.0	152.6	130	119.7	119.4
70	...	149.5	148.7	140	113.6	112.8
80	...	146.0	144.6	150	107.2	105.6
90	...	142.5	140.2	160	100.4	
100	135.6	138.5	135.6	170	93.3	
110	130.7	134.0	130.6	180	85.8	
120	125.3	129.0	125.3			

[a] The highest temperature at which experimental measurements were made was 67° F.

Published data (*10, 11, 14*) relating to the isobaric heat capacity and the isothermal enthalpy-pressure coefficient of saturated liquid and gaseous propane permit the calculation of the change in the latent heat of vaporization with temperature by means of the following equation:

$$L = L_A + \int_{T_A}^{T} \left\{ C_{P_d} - C_{P_b} + \left[\left(\frac{\partial H}{\partial P}\right)_{T_d} - \left(\frac{\partial H}{\partial P}\right)_{T_b} \right] \frac{dP''}{dT} \right\} dT \qquad (2)$$

Table II includes values of the latent heat of vaporization based upon Equation 2 and the experimentally determined value of the latent heat at 100° F., which was taken as the reference value, L_A. The agreement between the experimental results and those calculated from Equation 2 is satisfactory when it is considered that they are based primarily upon different types of experimental measurements.

The latent heat of vaporization of *n*-pentane was determined experimentally at fourteen temperatures between 80° and 200° F. The individual experimental results are recorded in Table I*B*, together with smoothed values obtained by residual interpolation. The deviations of the experimental values from the smoothed data are also included. These measurements are somewhat more consistent than were the values for propane, the average deviation of the experimental values from the smoothed data being only 0.22 per cent. This improved accuracy is to be expected since *n*-pentane was farther below its critical temperature under these conditions than was propane, and therefore the heat of vaporization was larger and the correction terms were much smaller.

Smoothed values of the latent heat of vaporization of *n*-pentane at even temperatures are recorded in Table III. For comparison, values of the latent heat of vaporization calculated by Young (*15*) from his volumetric data are included. The latter results were interpolated by residual methods to the even temperatures recorded in Table III. The agreement between the experimental results and the values reported by Young is considered satisfactory, although the discrepancies at some temperatures are larger than the estimated experimental uncertainty in the present measurements.

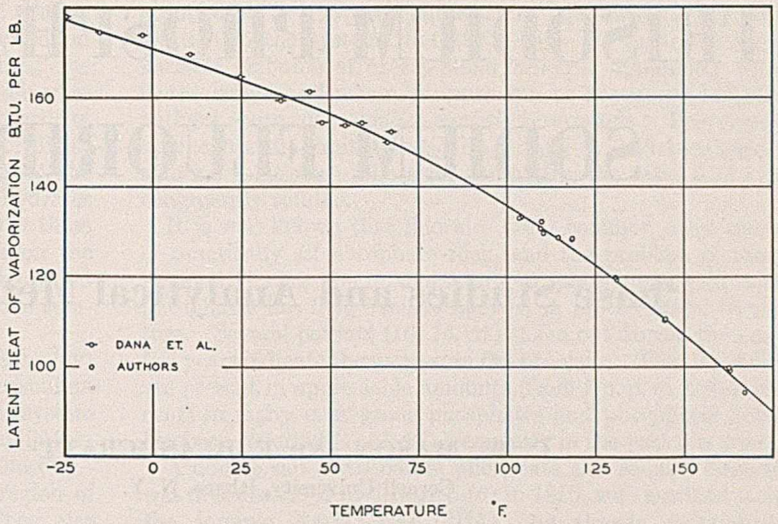

FIGURE 3. LATENT HEAT OF VAPORIZATION FOR PROPANE

TABLE III. COMPARISON OF LATENT HEAT OF VAPORIZATION RESULTS FOR *n*-PENTANE

Temp. °F.	Exptl., Authors	Exptl., Griffiths and Awbery	Clapeyron Equation, Young	Equation 2, Authors
	B. t. u./lb.			
60	...	158.3	...	161.3
70	...	156.0	...	159.3
80	156.2	153.6	155.8	157.3
90	154.7	151.2	154.0	155.3
100	153.2	148.8	152.2	153.2
110	151.5	...	150.2	151.1
120	149.7	...	148.2	148.9
130	147.7	...	146.2	146.6
140	145.6	...	144.0	144.3
150	143.3	...	141.7	141.8
160	140.9	...	139.4	139.3
170	138.4	...	137.0	136.7
180	135.9	...	134.5	134.1
190	133.2	...	132.0	131.3
200	130.4	...	129.3	128.4
210	...	...	126.6	125.4
220	...	...	124.0	122.3
230	...	...	120.9	119.1
240	...	...	118.0	115.8
250	...	...	115.0	112.4

Griffiths and Awbery determined experimentally the latent heat of vaporization of a commercial pentane, consisting primarily of *n*-pentane, at temperatures from −4° to 86° F. A part of the results of their experimental work is included in Table III. In general, they obtained values of the latent heat of vaporization which were approximately 6 B. t. u. per pound less than the values based either upon Young's volumetric data or upon the experimental measurements reported from this investigation. Within the accuracy of the Griffiths and Awbery measurements, they found a linear variation in the latent heat of vaporization with temperature.

The isobaric heat capacity and the isothermal enthalpy-pressure coefficient for saturated liquid and gaseous *n*-pentane (*4*, *9*, *12*, *14*) were used in conjunction with Equation 2 to evaluate the change in the latent heat of vaporization with temperature. The experimental result at 100° F. was taken as a reference point in calculating the values based upon Equation 2 which are recorded in Table III. The agreement of these values with those measured directly is considered satisfactory.

It is difficult to estimate with accuracy the absolute uncertainty involved in the experimental results reported in this paper. The precision of the directly measured quantities was distinctly better than the consistency of the final experimental results. This difference is probably due to traces of condensation in the packing of the motor-operated valve and possibly to entrainment of small particles of unvaporized liquid in the gas stream from the calorimeter. It is believed, however, that the values for the latent heat of vaporization of propane recorded in Table II do not involve any absolute uncertainty greater than 1.5 per cent. The values for *n*-pentane reported in Table III are somewhat more accurate and probably do not involve an uncertainty greater than 1 per cent. The errors of measurement of the primary quantities and of evaluation of the correction terms taken together were approximately 0.4 per cent in each case.

Acknowledgment

This work was done as a part of a general program of research relating to the thermodynamic behavior of hydrocarbon mixtures, which is being carried out by Research Project 37 of the American Petroleum Institute. The financial assistance and cooperation of the institute are appreciated. Lee T. Carmichael was of great assistance in connection with the construction and operation of the calorimeter.

Nomenclature

L = heat of vaporization, B. t. u./lb.
V_d = specific volume of saturated gas, cu. ft./lb.
V_b = specific volume of saturated liquid, cu. ft./lb.
Q_e = electrical energy added to calorimeter, B. t. u.
Q = energy lost from calorimeter due to temperature differences between it and the surroundings, B. t. u.
Δm = change in weight of contents of calorimeter, lb.
T = absolute temperature (thermodynamic scale), ° F. abs.
P = pressure, lb./sq. in. abs.
P'' = vapor pressure, lb./sq. in. abs.
H = enthalpy, B. t. u./lb.
C_{P_d} = isobaric heat capacity of saturated gas, B. t. u. /lb./° F.
C_{P_b} = isobaric heat capacity of saturated liquid, B. t. u. / lb./° F.

Literature Cited

(1) Beattie, Kay, and Kaminsky, *J. Am. Chem. Soc.*, 59, 1589 (1937).
(2) Dana, Jenkins, Burdick, and Timm, *Refrig. Eng.*, 12, 387 (1926).
(3) Griffiths and Awbery, *Proc. Phys. Soc.* (London), 44, 121 (1932).
(4) Kennedy, Sage, and Lacey, IND. ENG. CHEM., 28, 718 (1936).
(5) Osborne, *Bur. Standards J. Research*, 4, 609 (1930).
(6) Osborne, Stimson, and Fiock, *Ibid.*, 5, 411 (1930).
(7) Osborne and Van Dusen, U. S. Bur. Standards, *Sci. Paper*, 315 (1919).
(8) Rose-Innes and Young, *Phil. Mag.*, [5] 47, 353 (1899).
(9) Sage, Backus, and Vermeulen, IND. ENG. CHEM., 28, 489 (1936).
(10) Sage, Kennedy, and Lacey, *Ibid.*, 28, 601 (1936).
(11) Sage and Lacey, *Ibid.*, 27, 1484 (1935).
(12) Sage, Lacey, and Schaafsma, *Ibid.*, 27, 48 (1935).
(13) Sage, Schaafsma, and Lacey, *Ibid.*, 26, 1218 (1934).
(14) Sage, Webster, and Lacey, *Ibid.*, 29, 1309 (1937).
(15) Young, *Sci. Proc. Royal Dublin Soc.*, 12, 374 (1910).

TRISODIUM PHOSPHATE–SODIUM FLUORIDE

Phase Studies and Analytical Methods

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IN THE manufacture of commercial trisodium phosphate, the caking of the product due to the formation of a mat by the needlelike crystals of the dodecahydrate is a serious problem (*42*). A small admixture of fluoride has been used to give a product consisting mainly of octahedral crystals, the granular character of which improves the physical properties of the product. The nature of these crystals has been in question, and they have been considered to be either a double salt of sodium phosphate and sodium fluoride, or else sodium phosphate decahydrate.

It seemed questionable whether the latter hydrate actually existed or whether a double salt containing sodium fluoride (a persistent impurity in phosphate) had been repeatedly mistaken for it even in supposedly pure materials. It was also possible that here was a case of the stabilization of a metastable phase by adsorption of some impurity (possibly fluoride ion) which would prevent the crystallization of the stable hydrate. It can be stated at the outset that, although fluoride is apparently strongly adsorbed by trisodium phosphate dodecahydrate, no stabilization of any lower hydrate has been observed.

Trisodium phosphate decahydrate was first described by Rammelsberg (*34*) in 1865. He prepared it in the form of colorless, transparent, regular octahedra by recrystallizing small red and yellow crystals which were sometimes obtained as an impurity in the manufacture of soda. Later (*35*) he reported that this compound contained fluorine. In 1885 Baker (*3*) prepared and analyzed trisodium vanadate decahydrate, isometric octahedra and dodecahedra; he stated that, although they had not been prepared in any quantity, the isomorphous arsenate and phosphate could be demonstrated microscopically. Continuing Baker's work, Hall (*20*) gave details of a method for preparing trisodium arsenate decahydrate but did not succeed in obtaining the corresponding phosphate.

More recently Salkowski (*39*) claimed to have prepared a trisodium phosphate decahydrate by treating a 10 per cent solution of potassium, sodium, or ammonium dihydrogen phosphate with 0.3 to 0.4 volume of sodium hydroxide solution of density 1.34 and recrystallizing the product from water. Westbrook (*45*) patented a process for the preparation of the decahydrate in which a solution with the composition $1Na_3PO_4:10H_2O$ is held above its crystallization temperature and seeded with the decahydrate, and the crystals formed of the latter are removed. Mason (*8*, *49*) determined the refractive index of octahedra and dodecahedra obtained by crystallization of a warm trisodium phosphate solution on a microscope slide, and reported the compound as the decahydrate. Cross (*11*) later pointed out that the refractive index given for the decahydrate is the same as that of a double salt containing fluoride, $2Na_3PO_4.NaF.19H_2O$, which crystallizes in colorless octahedra and dodecahedra and which, in view of the small molecular weight of sodium fluoride, would analyze at about $Na_3PO_4.10H_2O$ if the presence of fluoride were unsuspected.

Besides the decahydrate and the well-known dodecahydrate, the following hydrates of trisodium phosphate have been reported: $Na_3PO_4.8H_2O$ (*29*, *34*), $Na_3PO_4.7H_2O$ (*20*), $Na_3PO_4.6H_2O$ (*29*), and $Na_3PO_4.{}^1/_2H_2O$ (*29*). The crystallographic descriptions of these are meager but are sufficient to prevent their being mistaken for the isometric octahedra or dodecahedra ascribed to the 10-hydrate. Apparently the only x-ray work done on any of the trisodium phosphates is shown by some recently published diagrams (*29*) of powder photographs of the 12-, 8-, 6-, and $^1/_2$-hydrates without comments as to the possible lattice types. Several authors have determined a transformation temperature at about 70° C. but have not described the new phase (*19*).

Because of the rather pronounced hydrolysis of trisodium phosphate solutions (*19*, *28*, *42*), it is necessary in investigating the various hydrates to consider the three-component system, $Na_2O–P_2O_5–H_2O$. This system was first investigated by D'Ans and Schreiner (*14*). They determined a transition temperature for trisodium phosphate dodecahydrate at 70.75 ± 0.1° C. (but did not give the transition product) and gave data for the 25° C. solubility isotherm within the limits 7.31–1.56 moles sodium and 6.40–0.040 mole phosphate per 1000 grams solution. Within this region the trisodium salt appeared in the solid phase only as the dodecahydrate. The composition of the solution in equilibrium with the dodecahydrate extended from the highly alkaline side (4.28 moles sodium, 0.040 mole phosphate per 1000 grams solution) through the solution having the 3:1 ratio of sodium to phosphate, and a little beyond to the slightly acid, invariant solution (3.48 moles sodium, 1.33 moles phosphate per 1000 grams solution) in equilibrium with both trisodium phosphate dodecahydrate and disodium phosphate dodecahydrate.

Smith (*41*) published a paper in 1917 on the constitution of the alkali phosphates. The facts that only ratios of sodium to phosphorus (or of Na_2O to Na_3PO_4) were considered in this paper and that the water of hydration was usually not determined have led to some misconceptions in the literature. Both Mellor (*28*) and Gmelin-Meyer (*19*) refer to Smith's work under the preparation of anhydrous trisodium phosphate. Smith was not able under any conditions to prepare a product having the simple ratio sodium:phosphorus = 3:1. When the crystals were free of the disodium salt, they invariably carried excess alkali and he concluded that the purest possible product had the molar ratio $Na_3PO_4:Na_2O = 18:1$, corresponding to 2.1 per cent Na_2O on a dry basis. Recent work tends to confirm these results.

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During the past decade patents have been issued dealing with methods of manufacturing and purifying trisodium phosphate (*10*, *15*, *27*). That a product containing the ratio sodium:phosphorus = 3:1 is not readily obtained is attested by patents (*5*, *43*) which have to do with methods of obtaining neutral trisodium phosphate. The ratio of di- to tri- salt in the product is not mentioned. Several of the patents (*9*, *24*, *45*) claim methods of preparing lower hydrates although it is not stated in the abstracts whether or not these are definite phases. The methods are all based upon the reaction of concentrated phosphoric acid or feebly hydrated di- or mono- salt with concentrated sodium hydroxide solution.

Recently a comprehensive article by Menzel and Sahr (*29*) cleared up some of the difficulties concerning the trisodium phosphates. They studied the 20° C. isotherm of the system $Na_2O-P_2O_5-H_2O$, from the invariant solution in equilibrium with the two solid phases, $Na_2HPO_4.12H_2O$ and $Na_3PO_4.12H_2O$, to a concentration in the highly alkaline region of 32.58 per cent Na_2O and 0.12 per cent P_2O_5. They also studied the solid phases obtained by the isobaric decomposition of the dodecahydrate and those in equilibrium with the solution of about the 3:1 ratio of sodium:phosphorus at elevated temperatures. Reference has already been made to the hydrates which were found by these authors. No decahydrate was mentioned and none of the descriptions given corresponded with regular octahedra or dodecahedra. With the exception of a determination of 50° C. and a solution composition of 3.49:1:90.44 $Na_2O:P_2O_5:H_2O$, their investigations did not extend into the region of high alkalinity and high temperature. This paper also brings out the hitherto unsuspected fact (it might have been suspected from the work of Smith, *41*, to which no reference is made) that trisodium phosphate dodecahydrate having the ratio sodium:phosphorus = 1:3 does not exist in equilibrium with any solution in the system $Na_2O-P_2O_5-H_2O$. It separates with variable amounts of excess alkali which is apparently held in the lattice and whose presence can be accounted for, the authors claim, on *räumlich-statistische* grounds. The excess approaches the limiting ratio $Na_2O:P_2O_5$ = 3.25:1 in highly alkaline solutions. The solid containing the ratio 3.22:1 is congruently soluble.

The supposed octahedral $Na_3PO_4.10H_2O$ is shown by analysis and by phase studies to be the double salt $NaF.2Na_3PO_4.19H_2O$. This phase may appear in samples of trisodium phosphate containing as little as 0.1 per cent sodium fluoride, an amount of impurity not uncommon.

Depending upon temperature, within limited regions of the ternary diagram either the octahedral double salt or the dodecahydrate may be the solid phase. A new isotropic phase, stable in alkaline phosphate solution at 75–90° C., is reported.

Data showing that the fluoride ion is either strongly adsorbed on or contained in solid solution in trisodium phosphate dodecahydrate are presented. Analytical methods for the determination of small amounts of fluorine in the presence of phosphate are reviewed, and modifications of the volumetric thorium nitrate procedure are suggested.

It is well known that fluorides are a common constituent of practically all phosphate rock, and the problem of their removal during the manufacture of phosphoric acid and phosphates has long been recognized in the technical literature. Several patents (*10*, *15*, *27*) taken out during the past few years indicate the interest in the problem. That fluorides are present in appreciable amounts (from 5 p. p. m. to 0.1 per cent) in many c. p. grade phosphates and phosphoric acids has been reported (*1*, *21*, *36*) frequently in the past few years.

A double salt of trisodium phosphate and sodium fluoride was first described by Briegleb (*6*) in 1856, who ascribed to it the formula $Na_3PO_4.NaF.12H_2O$. As already mentioned, Rammelsberg (*35*) reported fluorine in the octahedra which he had previously described as trisodium phosphate decahydrate. These octahedra from the soda manufacture were later examined by Baumgarten (*4*) who obtained from them on recrystallization the compound to which he ascribed the formula $2NaPO_4.NaF.19H_2O$. Later both Thorpe (*44*) and Baker (*3*) confirmed this composition.

The various investigators, all working on crystals described as regular octahedra, were almost certainly dealing with the same compound, of which $2Na_3PO_4.NaF.19H_2O$ is the correct formula. This is confirmed by the recent work of Neuman (*30*) who has described the space lattice and unit cell for the compound. No other double salts of sodium fluoride and trisodium phosphate have been reported.

Preliminary Experiments

The relation between fluorine content and phases separating from sodium phosphate solutions was established by a series of crystallizations which were studied microscopically. The octahedra whose refractive index was given by Mason (*8*, *49*) had been obtained by crystallization of "c. p." trisodium phosphate dodecahydrate from warm solutions; they were reproducible with two lots of trisodium phosphate dodecahydrate which had been in the laboratory stock for a number of years. Trisodium phosphate samples, prepared in the laboratory from c. p. phosphorus pentoxide or from burning c. p. yellow phosphorus, gave no octahedra or other isotropic crystals. Recently purchased c. p. trisodium phosphates also failed to give octahedra.

Mixtures of sodium fluoride and trisodium phosphate (reagent grade), in the double salt ratio $2Na:PO_4:NaF$ (5.2 per cent NaF) gave large, well-formed octahedra. These solutions could be evaporated to dryness either slowly or rapidly without the formation of any anisotropic material. Quite often when an excess of fluoride was present, the octahedra were not so well formed and their faces had a rough appearance. Solutions containing an excess of the phosphate always gave the characteristic needles (hexagonal prisms) of the dodecahydrate along with the octahedra. It was not possible to judge accurately at what ratio the needles began to come out first because of the tendency of the solutions to supersaturate and because of the rapid evaporation at the edges of the preparation. When the percentage of sodium fluoride was low, the behavior of the solutions was similar to that of the phosphate preparations previously studied by Mason; that is, octahedra (and dodecahedra) were obtained only from warm, concentrated solutions. When the sodium fluoride, computed on the basis of the weight of solid dodecahydrate, amounted to about 0.57 per cent, octahedra were still easily obtained at room temperature and were judged to be present in the preparation in excess. At 0.34 per cent sodium fluoride the octahedra were easily obtained by warming; at 0.11 per cent they were obtained only with difficulty and in small quantity even by warming; and at 0.05 per cent only twice out of a number of trials were single, thin, isotropic dendrites obtained. Evidently the presence of isotropic octahedra on recrystallization is a fairly sensitive indication of the presence of fluoride in trisodium phosphate.

Attempts to seed a saturated solution of the composition $Na_3PO_4.10H_2O$ with crystals of the double salt yielded no additional crystals of isotropic material. Various other attempts at crystallization in the absence of fluoride gave only anisotropic crystals.

As mentioned above, the obvious place to look for a trisodium phosphate decahydrate in stable equilibrium is in alkaline solution at temperatures above 25° C. The exploratory work was limited to a systematic microscopical study, as follows:

Standard solutions of trisodium phosphate (containing less than 2 p. p. m. fluorine based on the solid dodecahydrate) and carbonate-free sodium hydroxide (up to 30 per cent excess) were prepared. The latter was kept in a paraffin-lined bottle. A drop of the phosphate solution was placed on a slide and to this was added a drop of the hydroxide solution either directly or after evaporation of the original drop according to the concentration desired. The hydroxide was added as rapidly as possible, and the preparation was immediately covered with a cover glass. Since the concentrated solution pressed out around the edge of the cover glass quickly solidifies, the rather permeable seal thus formed both decreases the rate of diffusion and prevents the carbon dioxide from the air from diffusing into the main body of the solution during the time of observation (15 to 30 minutes). The preparations were next placed in a hot stage for observation at the desired temperatures.

By these methods it was discovered that a new isotropic phase is formed, apparently under equilibrium conditions, when a preparation containing 25–35 per cent Na_3PO_4 and 10–15 per cent NaOH (10–15 per cent P_2O_5, 25–30 per cent Na_2O) is held at temperatures of from 75–90° C. No attempt was made to determine the limits within which the phase is stable; those given are merely limits within which it is easily obtained. The characteristic habit of the crystals is bladed dendritic. Clusters of six blades radiating at right angles from a point are quite common. Frequently the crystals which form on the surface of the slide appear to be very tiny octahedra, but the larger specimens are invariably bladed forms. When a preparation containing this isotropic phase is cooled to room temperature, it is seen to be unstable. Usually spontaneously (always after seeding) the needles of the dodecahydrate begin to grow slowly through the preparation; the isotropic crystals meanwhile plainly dissolve among the tangled mat of needles.

The refractive index of the isotropic phase was determined by immersing a good preparation in absolute alcohol, lifting the cover glass, and moving the slide about to remove the water. Crystals isolated in this manner still transformed rather rapidly to anisotropic pseudomorphs both in the alcohol and the immersion liquids. However, by using a number of preparations it was possible to fix the refractive index at approximately 1.465 ± 0.003. That the isotropic phase is not the same as the double salt, $2Na_3PO_4.NaF.19H_2O$, was definitely established by placing crystals of both together in a liquid of refractive index 1.460. The index of the double salt is lower whereas that of the new isotropic crystals is higher than that of the liquid.

Although precaution had been taken to exclude carbonates, preparations with added sodium carbonate were crystallized as described above, but none yielded any isotropic phase. It seems reasonable to conclude that the isotropic phase is a lower hydrate of trisodium phosphate with less than 12 molecules of water, but its composition and the precise conditions for its formation and stability remain to be studied quantitatively.

The System Na_3PO_4–NaF–H_2O

Before the quantitative examination of the system Na_3PO_4–NaF–H_2O was begun, it was realized that, at least over the whole range, it could not be looked upon as a true three-component system. This is due to the fact that trisodium phosphate dodecahydrate crystallizes with variable contents of excess alkali (*29*). However, it was thought probable from the work of Menzel and Sahr that the variations would be so slight as to escape detection by most types of observations and that the results would be of some practical value. The deviations from "three componency" would be manifest by the dependence of the composition of the "invariant" solution having $Na_{3+}PO_4.12H_2O$ as one solid phase on the ratio of the total amounts of the components present. (The 3+ signifies that the compound actually contains a little sodium in excess of that given by the stoichiometric formula, *29*.) As expected, the deviations were too small to be detected by the analytical methods used.

In general, the procedure used followed the well-known methods for investigating the phase relations of solid-liquid systems. Much time was saved by identifying the solid phases microscopically. This system is an ideal example for emphasizing the value of such a method. It could be used because the crystal properties of the solid phases expected were known. Because of the difficult and tedious analytical work required, and because of the necessity for frequent observations to ensure equilibrium conditions, it was estimated that the work was done in less than a third of the time which would have been required for methods based wholly on indirect analysis.

The following chemicals were used in the preparation of the solutions: trisodium phosphate and sodium fluoride, reagent grade (General Chemical Company); phosphoric acid, 85 per cent, U. S. P., sirupy (American Agricultural Chemical Company); distilled water.

The solutions were made up in large Pyrex test tubes, and repeated additions of the various components made until the desired solid phase was achieved. The solutions were heated to such a temperature that all, or nearly all, of the solid dissolved and were then cooled slowly with frequent stirring to the temperature of investigation. They were then seeded with small crystals of the phases which might be expected. The tubes were closed with tight-fitting, cleaned rubber stoppers and were kept in a constant-temperature (±0.1° C.) bath for 2 weeks or more before the first analysis was made. During this time the tubes were shaken several times daily and were subjected intermittently to temperatures 1–2° C. above and below the temperature of investigation. Immediately before analysis, the tubes, with the stoppers wired on, were shaken for about 24 hours. These precautions were necessary since the system is quite prone to supersaturation effects. Analysis of second samples taken several days after the first showed that equilibrium had been reached.

Samples for analysis were removed from the tubes through a fine glass wool filter by means of a pipet. They were transferred to weighing bottles and weighed immediately. Samples of the solid phase were removed and examined microscopically whenever samples of the solution were taken. Some difficulty was found in taking samples from solution 3 at 25° and from solution 4 at 40° C. Solution 3 had a tendency to hold some of the solid in suspension in a finely divided form, and this could be eliminated only by allowing it to settle undisturbed a day or two before sampling. At 40° C. it was difficult to remove the sample without some crystallization on the walls of the pipet unless the latter was warmed.

Table I summarizes the analytical data. Since the system is not truly three component, solution 1, containing three solid phases, was included. This solution should be truly invarient in the four-component system $NaOH-H_3PO_4-NaF-H_2O$. Since the solid phases found here are representative of those found throughout the system with the exception of sodium fluoride, a photomicrograph is shown in Figure 1. Much of the material is in fragmental form, but typical crystals of the three phases are easily recognized. Although in the case of solutions 2 and 3 the sodium:phosphorus ratios fall slightly below 3:1, as would be expected from the work of Menzel and Sahr (*29*), the difference is very slight (the results recorded are subject to the analytical error to be mentioned later, which would tend to raise them); and for practical purposes solution 3 may be considered invariant. In the cases where the values for sodium fluoride are given to only one significant figure, the results were obtained by the colorimetric method and are presented merely as confirmatory evidence of the small amounts present.

Solution 2 showed the same behavior of the double salt octahedra as had been observed in the microscopic work. It was originally thought to be the invariant solution 3, but several days after preparation the octahedra were evidently dissolving and within a week were completely gone. When the solution was warmed to about 50° C., the solid phase changed from 100 per cent dodecahydrate to 100 per cent octahedral double salt. At about 40° C. both phases were present so that the solution was brought to equilibrium at that temperature and analyzed. It is evident from the large decrease in the fluoride content of the solution (from 0.3 per cent at 25° to 0.02 per cent at 40° C.) that the solubility of the double salt decreases rapidly with rising temperature in the range 25–40° C., as long as the solution remains saturated with respect to phosphate. The same would almost certainly be true at lower and most probably at somewhat higher temperatures.

Figure 2 is a diagram of the system prepared from the data of Table I. Figure 3 is a type diagram which has been distorted in order to illustrate certain points more clearly. The coordinates (per cent NaF and per cent Na_3PO_4) of various points are included in Figure 3 for reference. Corresponding points of the two diagrams are designated by the same letters.

The diagrams are of the usual type for the representation of the isothermals of three-component systems where the percentages by weight of the three components are plotted along the three sides of an equilateral triangle. All lines shown are boundary lines which separate regions in which the number and composition of phases are different. Any composition to the left of line *ABCD* will give a single phase (a solution); compositions to the right of this line and to the left of *EFH* (Figure 3 only) will give both a liquid (solution) phase and one or two solid phases. Regions to the right of *EFH* will be completely solid.

In the region *ABE* the solid phase is trisodium phosphate dodecahydrate. Line *AB* shows the comparatively large decrease in the solubility of the phosphate upon the addition of small amounts of fluoride. A similar decrease on addition of chloride has been reported (*31*).

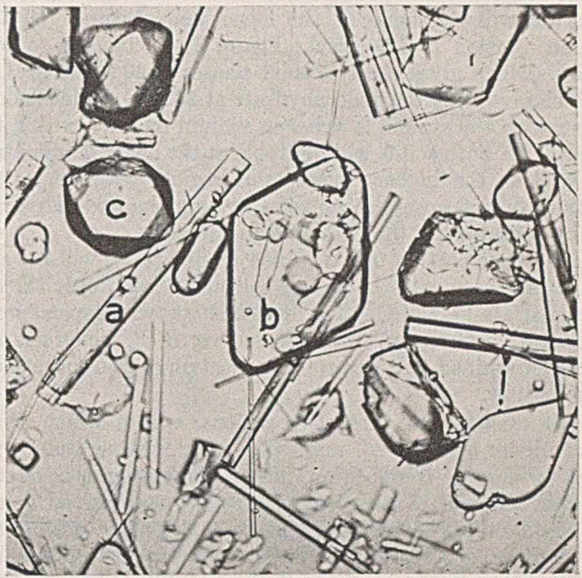

FIGURE 1. PHOTOMICROGRAPH OF THE SOLID PHASES

a. Hexagonal prisms, $Na_3PO_4.12H_2O$
b. Monoclinic rhombs, $Na_2HPO_4.10H_2O$
c. Regular octahedra, $NaF.2Na_3PO_4.19H_2O$

Compositions in the region *BEF* give two solid phases, the dodecahydrate and the double salt, and the invariant solution *B*. In *BCF* there is again only one solid phase (the double salt) in equilibrium with solutions whose compositions are given by line *BC*. At *C* is another invariant solution, and within *CHF* the phases are solution *C*, double salt, and sodium fluoride. In *CDH* the only solid phase is sodium fluoride, and line *DC* represents the decrease in its solubility on addition of phosphate.

TABLE I. EQUILIBRIA AT TWO TEMPERATURES

Solution No.	Total Composition, % by Wt.			Solid Phases (Microscopically)	Solution Composition, % by Wt.				Molar Ratio $Na_2O:P_2O_5$
	NaF	Na_3PO_4	H_3PO_4		P_2O_5	Na_2O	Na_3PO_4	NaF	
					At 25° C.				
1	1.1	23	2.0	$Na_3PO_4.12H_2O$ $Na_2HPO_4.12H_2O$ $2Na_3PO_4.NaF.19H_2O$	$\left.\begin{matrix}7.00\\7.17\end{matrix}\right\}7.09$	$\left.\begin{matrix}6.41\\6.60\end{matrix}\right\}6.51$	..	0.012 0.02 0.02	$\left.\begin{matrix}2.09\\2.10\end{matrix}\right\}2.10$
2	0.17	15.3	...	$Na_3PO_4.12H_2O$	$\left.\begin{matrix}3.94\\4.14\end{matrix}\right\}4.04$	5.28	9.33	0.04 0.048	2.85
3	1.6	17.2	...	$Na_3PO_4.12H_2O$ $2Na_3PO_4.NaF.19H_2O$	$\left.\begin{matrix}3.10\\3.08\end{matrix}\right\}2.09$	$\left.\begin{matrix}3.95\\3.90\end{matrix}\right\}3.93$	7.14	$\left.\begin{matrix}0.317\\0.342\end{matrix}\right\}0.325$	$\left.\begin{matrix}2.92\\2.90\end{matrix}\right\}2.91$
4	0.83	6.5	...	$2Na_3PO_4.NaF.19H_2O$	$\left.\begin{matrix}1.39\\1.38\end{matrix}\right\}1.39$		3.22	0.412	
5	6.9	3.0	...	$2Na_3PO_4.NaF.19H_2O$ NaF	$\left.\begin{matrix}0.556\\0.531\end{matrix}\right\}0.544$		1.26	$\left.\begin{matrix}1.13\\1.05\end{matrix}\right\}1.09$	
					At 40° C.				
2′	0.17	15.3	...	$Na_3PO_4.12H_2O$ $2Na_3PO_4.NaF.19H_2O$	$\left.\begin{matrix}6.41\\6.30\end{matrix}\right\}6.36$		14.7	$\left.\begin{matrix}0.0239\\0.0243\end{matrix}\right\}0.0241$	
Solubility of Na_3PO_4 (*14*)				$Na_3PO_4.12H_2O$ (25° C.)			12.3	..	
Solubility of NaF (*32*)				NaF (25° C.)			..	3.97	

Point *B′* shows the position to which the invariant solution *B* shifts at 40° C. The phases to be found within area *B′FE* at 40° are the invariant solution *B′*, the double salt, and the dodecahydrate. The region of compositions within which double salt octahedra formed by heating (to 40° C.) will dissolve on cooling (to 25° C.) may be found direct from the diagram. It is the region *BXEB′*, common to two fields of the diagram: (*a*) to either the field *B′EF* or the field *B′C′F*, within which the double salt (with or without the dodecahydrate, respectively) will be stable at the higher temperature; and (*b*) to the field *BAE*, within which only the dodecahydrate will be stable at the lower temperature. Of this region, portion *B′XE* (black, Figure 3) is common to both *B′EF* (which gives the two solid phases at 40°) and to *BAE* (which gives only the dodecahydrate at 25° C.). Since above this region the system is richer in sodium fluoride, within the field *X′FE* both solids will be stable at the lower temperature as well as the higher; below this region, with very little sodium fluoride present, no solid or only the dodecahydrate will be obtained at the higher temperature.

The other portion, *BB′X* (lined in Figure 3), will have as the solid phase only the double salt at 40°, and only the dodecahydrate at 25° C. Its precise shape will depend upon the location of the 40° solubility curve, *B′C′*, which has not been determined, but no probable location of this curve could eliminate it.

The existence of these two regions, within which phase transitions depend so markedly upon temperature over such a narrow composition range, throws light upon the known behavior of supposedly pure and commercial grades of trisodium phosphate. The above study, while admittedly incomplete, can serve as a basis for interpreting and controlling the changes in the relative amounts of the various crystalline phases. A more detailed investigation of the system at 40° C. or higher temperatures, with definite location of the positions to which the various points *A′*, *C′*, *D′*, and solubility curves shift, would be in order but is not essential evidence for the explanations sought in the present investigation.

The authors' opinion, based on the evidence presented, is that in all cases in which a trisodium phosphate decahydrate has been described the substance really obtained was the double salt, $2Na_3PO_4.NaF.19H_2O$. This is due to the fact that many samples of supposedly pure phosphate have undoubtedly contained enough fluoride (0.1 per cent sodium fluoride) to cause the formation of the double salt at higher temperatures. Its observed instability at lower temperatures and in the presence of the dodecahydrate would naturally be interpreted, when the presence of fluorine was not suspected, as the behavior of a lower hydrate. Further, the analysis of the double salt for water by difference would, if the presence of fluorine were not suspected, give a value only 1.6 per cent higher than that of a decahydrate.

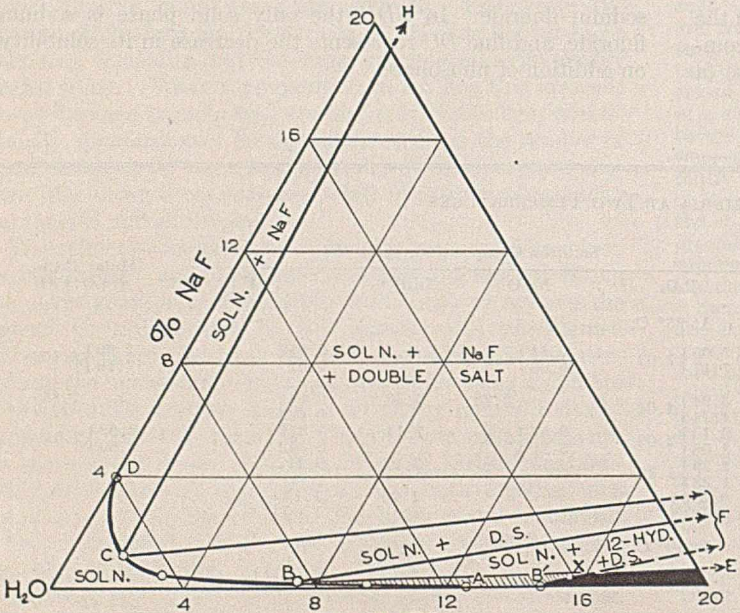

FIGURE 2. PART OF DIAGRAM FOR H_2O–Na_3PO_4–NaF SYSTEM AT 25° C.

It is believed that the other isotropic phase (the bladed dendrites) obtained at considerably higher temperatures is a lower hydrate which has not been reported previously.

Excess Fluoride in Solid

During the course of the investigation an anomalous behavior of the solutions whose solid phase is trisodium phosphate dodecahydrate was noticed. For instance, the fluoride found in the case of solution 2 is only about 25 per cent of that originally added. This suggested at once that another solid phase might be present, but a careful examination failed to reveal anything but the needles of the dodecahydrate. In order to obtain additional data concerning this behavior, three new solutions were prepared by neutralization with sodium hydroxide of phosphoric acid to which small amounts of a standard sodium fluoride solution had been added. Both the solid and the solution were analyzed. The results are as follows; similar results might be obtained either because of adsorption of fluoride ion on the dodecahydrate or because of the formation of a solid solution:

Soln. No.	Total Composition, % by Wt.		% NaF in Solid	% NaF in Liquid	Total Mg. NaF Added	Total Mg. NaF Found
	NaF	Na_3PO_4				
2	0.17	15.3	0.50[a]	0.048	..	..
6	0.0144	14.7	0.0268	0.00841	6.45	6.61
7	0.0104	16.1	0.0238	0.0030	4.30	4.44
8	0.00344	11.7	0.0111	0.000549	2.15	2.13

[a] Estimated.

Analytical Methods

The work of Menzel and Sahr (*29*) showed the necessity of determining both sodium and phosphorus when trisodium phosphate dodecahydrate is present as a solid phase, even if they were originally added in stoichiometric proportions.

A few preliminary trials of the volumetric method as used by Smith (*41*) and Menzel and Sahr (*29*) were first made, but it soon became apparent that the results depend greatly on the skill and experience of the operator. It was decided that a gravimetric method would give more reliable results in a shorter time.

The reagents used were made up from C. P. or reagent grade chemicals. The magnesia mixture was made up of $MgCl_2.6H_2O$ (50 grams per liter) and ammonium chloride (100 grams per liter), and acidified with hydrochloric acid. The double acetate reagent consisted of 32 grams of uranium acetate, 28 grams of magnesium oxide, 100 grams of glacial acetic acid, 500 ml. of 95 per cent alcohol, and water to make 1000 ml. The wash solution was made up of 95 per cent alcohol saturated with sodium magnesium uranyl acetate.

The sample in about 100 ml. was made acid to litmus with hydrochloric acid, and magnesia mixture. About 5 ml. in excess of the calculated amount were added. This was cooled in ice water and 1:4 ammonium hydroxide was added until it was neutral to methyl red. After formation of the precipitate, 15 ml. of concentrated ammonium hydroxide were added, and the solution was allowed to stand overnight. The precipitate was filtered through a previously ignited Gooch crucible, washed with 60 ml. of 1:19 ammonium hydroxide, dried at

110° C., placed in a muffle, and heated slowly to 1100°. In several trials a reignition resulted in a loss of weight of only 0.2 mg.

The filtrate from the phosphate precipitate was evaporated to about 20 ml. and made neutral to methyl red, and 2.5 ml. of the double acetate reagent were added for every milligram of sodium expected. After standing for an hour or more in the dark with frequent stirring, the precipitate was filtered through a Gooch crucible, washed several times with the wash alcohol, and dried at 110° C. A blank containing identical amounts of all reagents and wash solutions was run with each sodium determination. The factor used for conversion of the weight of precipitate to sodium is 0.0150 (*25*).

Fluorine must be removed from the solution before the magnesia precipitation is made (a solution containing 0.3 per cent sodium fluoride caused an error of about 25 per cent in the phosphate determination). This was done by repeated evaporation of the sample to dryness in platinum with concentrated nitric acid (*26*). In order that the magnesium ammonium phosphate precipitate may have the correct composition, it is necessary that the excess magnesia be carefully controlled (*26*). This is usually done by means of a second precipitation, but in the present work the amount of phosphate was known approximately from the preliminary run and the amount of magnesia could be calculated directly. When the phosphate precipitation is made from solutions containing much sodium, some magnesium sodium phosphate is precipitated (*26*). Because of the low sodium concentrations in the solutions analyzed, it is thought that this effect is small if not negligible. Such an effect would tend to make the phosphate results too high and the sodium too low and so would be magnified in the ratio sodium: phosphorus.

Preliminary runs were also necessary in order to know the amount of sodium present, for the amount in a determination must be limited to less than about 40 mg. of sodium oxide (*25*). Caley (*7*) puts the error to be expected in analyzing for such an amount at less than 0.7 mg.

As a test of the method a sample of Kahlbaum secondary sodium phosphate "for analysis" was analyzed. The water of crystallization in this compound, the dodecahydrate, is not constant but the molar ratio sodium:phosphorus should be very nearly 2:1. The results obtained for this ratio were 1.91 and 1.95. It is probable that at least part of this deviation from theoretical is due to the loss of sodium mentioned above.

By far the most difficult problem of the whole investigation was the development of a satisfactory technique for the determination of small amounts of fluorine. An integral part of the problem of determination is the separation of the fluorine from phosphates which were almost always present in large excess in the materials analyzed in this work. Even traces of phosphates interfere in any method for the determination of fluorine yet developed. The authors' belief is that several important and critical points in the methods of separation and determination have not been sufficiently stressed and perhaps not even recognized. That the methods in use are not immediately successful in the hands of different operators is evidenced by a recently published collaborative study (*12*). The results for the amount of fluorine in a standard sample of dicalcium phosphate reported by a group of thirty-five collaborators differed by a factor of 6.5 at the extremes and gave almost a linear distribution between these values.

The following methods appeared most promising: titration with thorium nitrate with sodium alizarin sulfonate indicator (*1*, *2*, *23*, *48*); precipitation as lead chlorofluoride (*22*) or triphenyl tin fluoride (*17*); colorimetric methods based on the bleaching of a solution of oxidized titanium (*47*) or zirconium–alizarin lake (*40*); and a spectrographic method (*33*). A consideration of the small amount of fluorine to be expected in some of the samples eliminated the lead chlorofluoride method. Precipitation as triphenyl tin fluoride was not attempted because of the unavailability of the reagent.

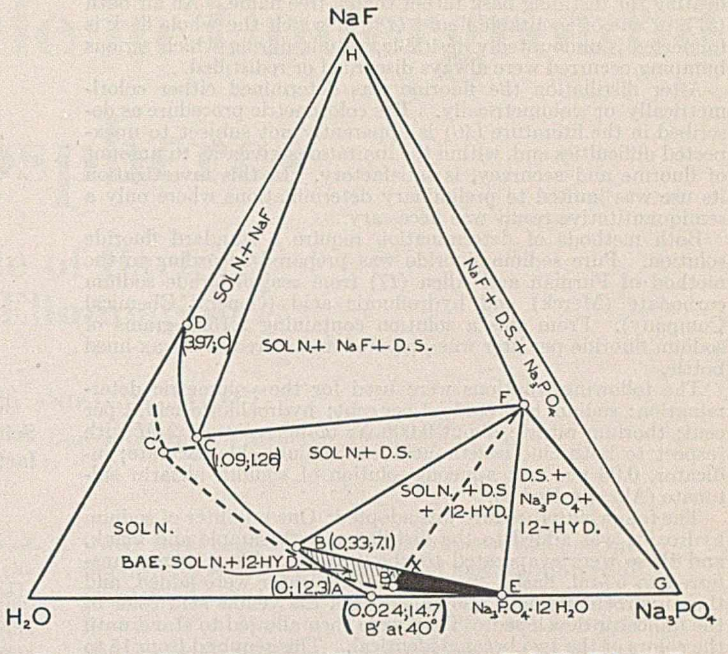

FIGURE 3. TYPE DIAGRAM (DISTORTED) OF H_2O–Na_3PO_4–NaF SYSTEM AT 25° C.

The oxidized titanium method was not tried because it seemed to offer no advantages over the zirconium–alizarin lake method unless a polarizing photometer was available. The manipulation of the quantitative spectrographic technique was rather laborious, and in some cases the samples to be analyzed were outside (both above and below) the range (*33*) to which the method is applicable.

The methods chosen for the present investigation were the thorium nitrate titration and the colorimetric method of Sanchis (*40*) based on bleaching of a zirconium–alizarin lake.

By far the most practical method for the separation of fluorine from nonvolatile substances is the distillation as fluosilicic acid from sulfuric or perchloric acid solutions, first used by Willard and Winter (*48*). This method was used in the present work, the procedure being modified to include recent improvements:

The apparatus consisted essentially of a steam generator, Claisen distilling flask, and Liebig condenser. The distilling flask was fitted with cleaned rubber stoppers, one of which carried a thermometer and a glass tube from the steam generator. Both the tube and the thermometer reached to the bottom of the flask. About a dozen glass beads were placed in the flask. The lower end of the condenser was fitted with an adapter whose end dipped below the surface of the distillate. Before each run the flask was cleaned with hot alkali to remove the siliceous coating which might retain some fluorine (*23*, *36*). Ten milliliters of freshly boiled sulfuric acid (*23*) were used for a distillation. This should result in 100 per cent recovery of fluorine when the distillation is carried out at 140° C. and 150 ml. are collected (*13*). As a precautionary measure 200 ml. were collected. The temperature was kept as close to 140° as possible by constant observation and control of the rate of distillation and of steam addition.

Failure to appreciate fully some of the critical factors governing the distillation seems to be largely responsible for failures in the determination of fluorine (*12*, *46*). One point which has not been sufficiently stressed is that, when large amounts of phosphate are present, some is distilled along with the fluorine (*36*). This, as well as the distillation of a little sulfuric acid (or some volatile impurity not removed by the previous boiling), was found to introduce appreciable error; to eliminate this, 400 ml. of distillate were always collected and the last 200 ml. were used as a blank. This entails strict control of the temperature and possibly of the rate of distillation. A difficulty with the distillation is the tendency for bumping which may introduce large errors by causing spray to be carried over. The bumping is overcome to a certain extent by the use of a bath of Crisco for heating the distilling flask rather than a free flame. An air bath (*37*), or one of a suitable liquid (*18*) in which the whole flask is immersed is undoubtedly desirable. Runs during which serious bumping occurred were always discarded or redistilled.

After distillation the fluorine was determined either colorimetrically or volumetrically. The colorimetric procedure as described in the literature (*40*) is apparently not subject to unexpected difficulties and, within the limitations given as to amount of fluorine and accuracy, is satisfactory. In this investigation its use was limited to preliminary determinations where only a semiquantitative result was necessary.

Both methods of determination require a standard fluoride solution. Pure sodium fluoride was prepared according to the method of Furman and Allen (*17*) from reagent-grade sodium carbonate (Merck) and hydrofluoric acid (General Chemical Company). From this a solution containing 2.1525 grams of sodium fluoride per liter was prepared and stored in a wax-lined bottle.

The following solutions were used for the volumetric determination: sodium hydroxide, 1 per cent; hydrochloric acid, 1 per cent; thorium nitrate, about 0.008 *N*; buffer solution, 2 *M* with respect to both chloroacetic acid and sodium chloroacetate; indicator, 0.05 per cent aqueous solution of sodium alizarin sulfonate (Alizarin Red S).

The following procedure was adopted: One milliliter of sodium hydroxide was added to the distillates, both sample and blank, and these were evaporated to about 10 ml. They were transferred to 50-ml. flasks, two drops of indicator were added, and then hydrochloric acid was added until the yellow acid color of the indicator developed. They were then allowed to stand until the colors of the two became identical. This required from 15 to 30 minutes and sometimes the addition of another drop of acid to the blank. Sodium hydroxide was then added until the indicator just turned, and the final acidification was made with nine drops of the buffer solution. As soon as the colors became identical, 10 ml. of 95 per cent alcohol were added. (It was the authors' experience that equally good results could be obtained without the use of alcohol. In this connection see the recent paper by Rowley and Churchill, *38*.) The blank was then titrated to a faint pink and the sample titrated to match. Some skill and experience on the part of the operator are necessary in matching the colors.

Two important points in this procedure have not been sufficiently stressed. Because of the lack of sharpness in the development of the color of the indicator, it is necessary to match the color with that of a blank rather than try to stop at the same color each time through color memory. [Eberz, Lamb, and Lachele (*16*) suggested the use of a permanent standard for judging the end point.] The distillation blank may also serve as the color matching blank since the amount of thorium solution equivalent both to the color developed and to the phosphate and sulfate distilled is to be subtracted from that used for the sample. Whenever the solutions have been concentrated in the presence of sodium hydroxide, it is necessary upon acidification to wait for the true acid color to develop. Failure to do so may lead to the addition of too much or too little acid and, in spite of the buffer solution, vitiation of the results by as much as 50 per cent. The cause of this is not known, but it is probably connected with the rate of loss of carbon dioxide; it might easily result in errors unless two solutions were treated at the same time. It is always more apparent in the blank where less of the alkali added is neutralized.

Some of the data bearing on the accuracy of the determinations are as follows:

STANDARDIZATION OF THORIUM NITRATE SOLUTION

	Ml. Th Soln.		Mg. NaF/Ml. Th Soln.
	Blank	Sample (cor.)	
0.5 ml. NaF soln.	0.13	2.74	0.393
0.5 ml. NaF soln.	0.11	2.75	0.393

EFFECT OF AMOUNT OF SULFURIC ACID DISTILLED

	Ml. Th Soln.	
	Blank	Distillate
200 ml. distillate	0.10	0.23

RECOVERY OF SODIUM FLUORIDE ON DISTILLATION

	Ml. Th Soln.		% Recovery
	Blank	Sample (cor.)	
0.5 ml. NaF soln.	0.33	2.70	98.2

ANALYSIS OF PHOSPHATES

	% NaF
C. P. trisodium phosphate dodecahydrate (old stock)	0.09
Reagent-grade trisodium phosphate dodecahydrate (General Chemical Co.)	0.0003
C. P. phosphoric acid (Victor Chemical Works)	0.0004

Acknowledgment

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Literature Cited

(1) Armstrong, IND. ENG. CHEM., Anal. Ed., 8, 384 (1936).
(2) Armstrong, *J. Am. Chem. Soc.*, 55, 1741 (1933).
(3) Baker, *J. Chem. Soc.*, 47, 353 (1885).
(4) Baumgarten, *Z. Chem.*, [N. S.] 1, 605 (1865).
(5) Booth and Gerber, U. S. Patents 1,700,972–3 (1929).
(6) Briegleb, *Ann.*, 1856, 95.
(7) Caley, *J. Am. Chem. Soc.*, 52, 1349, 4247 (1930).
(8) Chamot and Mason, Handbook of Chemical Microscopy, Vol. I, p. 346 (1931).
(9) Chemische Fabrik Budenheim A.-G., French Patent 722,989 (1931).
(10) Chemische Fabrik Budenheim A.-G., German Patent 626,732 (1936).
(11) Cross, L. H., private communication to E. M. Chamot, 1933.
(12) Dahle, *J. Assoc. Official Agr. Chem.*, 20, 188 (1937).
(13) Dahle and Wickmann, *Ibid.*, 19, 313 (1936).
(14) D'Ans and Schreiner, *Z. physik. Chem.*, 75, 101 (1911).
(15) Dorr Co., British Patent 431,812 (1935).
(16) Eberz, Lamb, and Lachele, IND. ENG. CHEM., Anal. Ed., 10, 259 (1938).
(17) Furman and Allen, *J. Am. Chem. Soc.*, 54, 4625 (1932).
(18) Gilkey, Rohs, and Hansen, IND. ENG. CHEM., Anal. Ed., 8, 150 (1936).
(19) Gmelin's Handbuch der anorganischen Chemie, 8th ed., Vol. 21, p. 895 (1928).
(20) Hall, *J. Chem. Soc.*, 51, 94 (1887).
(21) Harden, *Nature*, 134, 101 (1934).
(22) Hoffman and Lundell, *Bur. Standards J. Research*, 3, 581 (1929).
(23) Hoskins and Ferris, IND. ENG. CHEM., Anal. Ed., 8, 6 (1936).
(24) I. G. Farbenindustrie A.-G., French Patent 696, 360 (1930).
(25) Kahane, *Bull. soc. chim.*, 47, 382 (1930).
(26) Kolthoff and Sandell, "Quantitative Inorganic Analysis", 1936.
(27) Levermore, U. S. Patent 2,046,829 (1936).
(28) Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. II, p. 847 (1922).
(29) Menzel and Sahr, *Z. Elektrochem.*, 43, 104–19 (1937).
(30) Neuman, *Z. Krist.*, 86, 298 (1933).
(31) Obukhov and Nikhailova, *J. Applied Chem.* (U. S. S. R.), 8, 1149 (1935).
(32) Payne, *J. Am. Chem. Soc.*, 59, 947 (1937).
(33) Petrey, IND. ENG. CHEM., Anal. Ed., 6, 343 (1934).
(34) Rammelsberg, *J. prakt. Chem.*, 94, 237 (1865).
(35) Rammelsberg, *Monatsh. Akad. Bull.* 1880, 777.
(36) Reynolds, *J. Assoc. Official Agr. Chem.*, 18, 108 (1935).
(37) Reynolds, Kershaw, and Jacob, *Ibid.*, 19, 158 (1936).
(38) Rowley and Churchill, IND. ENG. CHEM., Anal. Ed., 9, 551 (1937).
(39) Salkowski, *Z. physiol. Chem.*, 69, 475–8 (1910).
(40) Sanchis, IND. ENG. CHEM., Anal. Ed., 6, 134 (1934).
(41) Smith, *J. Soc. Chem. Ind.*, 36, 420 (1917).
(42) Snell, IND. ENG. CHEM., 23, 470 (1931).
(43) Société des phosphates tunisiens, French Patent 655,616 (1928).
(44) Thorpe, *J. Chem. Soc.*, [2] 10, 660 (1872).
(45) Westbrook, U. S. Patent 1,711,707 (1929).
(46) Wichmann, *J. Assoc. Official Agr. Chem.*, 20, 168 (1937).
(47) Wichmann and Dahle, *Ibid.*, 16, 612 (1933).
(48) Willard and Winter, IND. ENG. CHEM., Anal. Ed., 5, 7 (1933).
(49) Winchell, "Microscopic Characters of Artificial Minerals", p. 269 (1931).

Carbon Monoxide in Underground Atmospheres

The Role of Bacteria in Its Elimination

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Tests are described showing that certain types of bacteria or microorganisms are present in anthracite gangway waters, sewage, and surface materials which have the ability of readily consuming hydrogen and carbon monoxide from gaseous mixtures.

The reactions appeared to consist largely of oxidation of the carbon monoxide to carbon dioxide and oxidation of the hydrogen to water. In the tests in which oxygen was present in the atmosphere, the carbon monoxide did not combine with the hydrogen to give methane and water vapor. Under favorable conditions certain anthracite-mine bacteria or microorganisms remove carbon monoxide at a rapid rate; for example, a gangway water from one anthracite mine contained enough bacteria to remove 1.7 volumes of carbon monoxide per volume of the water during a 20-day exposure period. The type and character of the bacteria that cause elimination of the hydrogen and carbon monoxide have not as yet been identified, but work on this phase of the investigation is now under way.

Because of these findings it is no longer safe to assume that anthracite-mine fires are extinguished when the atmospheres in sealed fire areas contain no carbon monoxide. Bacteria or other living microorganisms may be present which are able to eliminate the carbon monoxide as fast as it is generated by the fire.

DURING an investigation by the Bureau of Mines of combustible gases and explosions in underground chambers, manholes, and conduits it was observed that certain gases lose part or all of their hydrogen and carbon monoxide contents on passing through certain soils, especially those containing organic and sewage materials. The action was thought to be due to microorganisms. A study by the Bureau of Mines, now in progress, has confirmed the suggestion that microorganisms found in the water and sludge from certain manholes consume both carbon monoxide and hydrogen at a rapid rate; and they may eliminate these gases from manufactured gas within 10 to 30 days, depending upon the rate at which the microorganisms multiply while in contact with the gas.

Some time ago the authors investigated a rather extensive underground fire in one of the anthracite mines of Pennsylvania. The fire area, which comprised some 6 million cubic feet of space, was sealed; a complete record of the atmosphere behind the seals was obtained by taking samples of the atmosphere at frequent intervals and at different locations. A plot of the composition of the atmosphere against the time elapsed after sealing showed that the carbon monoxide content, although rather high 2 days after sealing, dropped rapidly and had disappeared within 20 days after sealing. The final disappearance of the carbon monoxide was determined by testing the atmospheres at the seals in the mine with a micro carbon monoxide indicator capable of indicating concentrations of 0.002 per cent of carbon monoxide. Although calculations showed that some leakage took place in the sealed area it could account for only part of the carbon monoxide that had disappeared in the 20-day period.

Two suggestions were offered for this high rate of carbon monoxide disappearance: (*a*) The carbon monoxide was oxidized at temperatures below 150° C. by either the anthracite or its ash (tests on many anthracites have shown that at temperatures above 150° C. carbon monoxide is liberated in the oxidation products when air is passed through it); (*b*) the carbon monoxide was consumed by microorganisms in the sealed area, as indicated in manhole surveys, if carbon-monoxide-consuming bacteria were present in the gangway water, on the decaying timber, or on the coal itself.

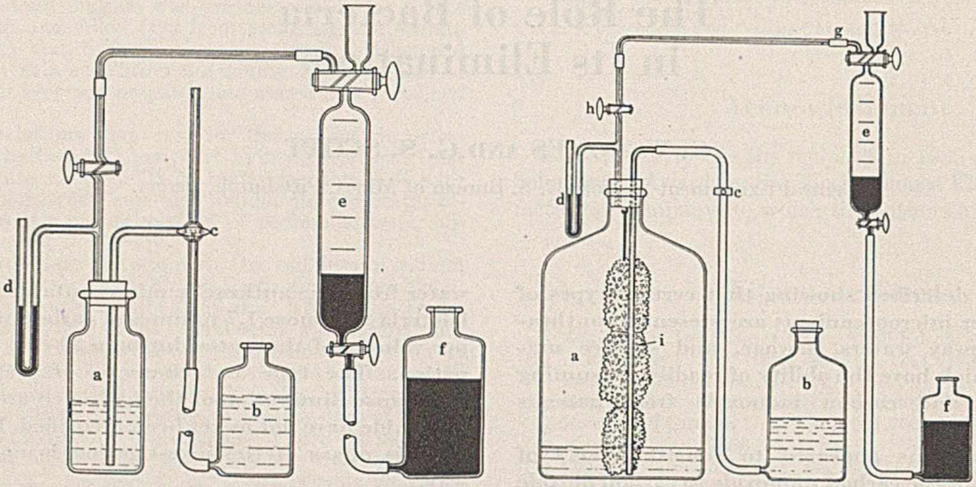
In many anthracite mines in Pennsylvania conditions are favorable for the harboring and growth of bacteria. Surface water containing various types of bacteria often passes through fissures and broken areas from the surface into the mine workings; various types of bacteria will be present in and around stables and along the gangway over which the mules travel; and there are microorganisms associated with the decay of mine timber.

That bacteria might be the cause of the carbon monoxide elimination in the area was indicated by Graham (*2*) who made oxidation experiments on wetted shavings from old pit props and found that the residual gas remaining after the experiments did not contain even a trace of carbon monoxide; however, he found that if zinc chloride was added to kill any bacteria that might be present, the oxidation was accompanied by the formation of carbon monoxide. These experiments showed that microorganisms may be instrumental in the elimination of carbon monoxide when wood is oxidized.

Haldane and Makgill (*3*) conducted an investigation to determine why carbon monoxide is absent in concentrated black damp from old workings. When they confined dry coal dust in a flask at 104° F. (40° C.) until the oxygen in the atmosphere disappeared (after 17 days), carbon monoxide was produced, and the quantity increased steadily as the oxygen was absorbed. The percentage of carbon monoxide liberated was 0.32 at the end of the experiment, but in similar tests on wetted coal dust with pure oxygen substituted for air a sample taken 20 hours after the start of the experiment contained 0.36 per cent carbon monoxide; on the third day the percentage had risen to 0.55 per cent, on the fourth day it had fallen to 0.41, and after 14 days the carbon monoxide had disappeared. These investigators suspected that bacterial action might be hastening the oxidation of wet coal and causing the disappearance of carbon monoxide; but further experimentation with a solution of mercuric chloride of 1 part in 1000 instead of pure water showed that the carbon monoxide disappeared after a time. As a result of these and numerous other tests they concluded "that bacteria did not cause the elimination of carbon monoxide, but that the disappearance of the carbon monoxide is due to the oxidizing action of the substance which is at first found in the coal when it takes up oxygen from the air . . . . and that if coal is wet when air is slowly passing over it, the carbon monoxide formed in its oxidation will disappear completely, so that we can thus easily account for the absence of carbon monoxide in the black damp issuing from old workings where the coal is nearly always wetted by water."

The experiments to be reported here show that in mine-fire atmospheres containing high percentages of carbon monoxide and hydrogen, both gases may be removed by microorganisms (bacteria) and that even when the atmosphere was not in contact with coal, the carbon monoxide was entirely eliminated and the hydrogen almost completely eliminated before the oxygen content of the atmosphere in contact with the microorganisms was reduced to zero. The results presented here indicate that bacteria may play a major part in the consumption of carbon monoxide and hydrogen in anthracite-mine fire areas, underground soil areas, and manholes used by utilities for power, light, and other services.

The authors have made no attempt as yet to identify the type of bacteria that causes the reactions at ordinary temperatures; however, enough selected and diverse materials have been tested to show that such carbon-monoxide-consuming bacteria are widely distributed and may perhaps be present in bituminous and other mines.



Figures 1 (*left*) and 2 (*right*). Reaction Vessel for Studying the Activity of Microorganisms on Gases

Effect of Bacteria on Carbon Monoxide

The disappearance of carbon monoxide in the particular sealed anthracite area was at first thought to be due to its absorption by the coal at temperatures below 150° C. A sample of 900 grams of 8–14 mesh anthracite was confined in a mercury-sealed bell jar containing 8.6 liters of an atmosphere with 1.10 per cent carbon monoxide for 5 months at laboratory temperatures. The slight decrease in the carbon monoxide content was insufficient to account for the disappearance of carbon monoxide in the sealed-mine fire area.

Atmospheres containing various percentages of carbon monoxide were passed through charges of anthracite at temperatures ranging from 150° C. to ordinary room temperatures to determine whether the carbon monoxide reacted catalytically with the heated coal or any of the mineral constituents in the coal ash; the results showed little if any reaction of the carbon monoxide.

As a preliminary experiment to determine the effect of bacteria on carbon monoxide, a sample of surface drain water from a storm sewer at the Central Experiment Station at Pittsburgh was placed in a test apparatus of the type shown in Figure 1. Reaction vessel *a*, previously sterilized at 100° C., was filled with distilled water by passing the water from leveling bulb *b* through cock *c* into the bottle. The connection between bottle *a* and mercury sampling bottle *e* was broken at *g*, and a gas mixture containing 0.52 per cent of carbon monoxide was added as the water was withdrawn completely from the reaction chamber. Three hundred cubic centimeters of the sewage were then run into the vessel from leveling bottle *b*, and the gas displaced by the liquid was allowed to escape to the air. The cock above manometer *d* was then closed, and samples were withdrawn through cock *h* for analysis at the end of 8 and 20 days, by means of sample bottle *e* and leveling bottle *f*.

The following change in composition of the gas mixture was observed (in per cent):

Days after start of test	0	8	20
Carbon dioxide	0.03	2.30	3.28
Oxygen	17.50	15.54	14.59
Hydrogen	0.00	0.00	0.00
Carbon monoxide	0.52	0.43	0.28
Methane	0.00	0.00	0.00
Nitrogen	81.95	81.73	81.85

The above results indicated that bacteria caused a very slow elimination of carbon monoxide and that other reactions caused the production of more carbon dioxide than would be produced by reaction of the bacteria with the carbon monoxide to produce carbon dioxide. These results were encouraging enough to try further experiments in which numerous types of bacteria would be present. A mixture of rotted wood, toadstools, fungi, and manure (materials that may be present in an anthracite mine) were stirred together in distilled water. A 300-cc. portion of the liquid and solid mixture was placed in reaction vessels of the type shown in Figure 1 in contact with an atmosphere made by the oxidation of anthracite with air at elevated temperatures. After 11 to 14 days the three atmospheres were analyzed and the following results were obtained (per cent by volume):

	Original Gas Mixture	Composition of Gas after: 11 days, bottle 2	13 days, bottle 3	14 days, bottle 1
Carbon dioxide	1.1	18.7	20.5	24.3
Oxygen	17.4	0.2	0	0
Hydrogen	3.3	0	0	0
Carbon monoxide	2.7	0	0	0
Methane	0.6	0.5	0.5	0.3
Nitrogen	74.9	80.6	79.0	75.4

Reactions were taking place in these mixtures even during the first day of test because of the reduction of pressure inside the bottles as indicated by the mercury manometers. In 11 days or longer the gas mixture which originally contained 3.3 per cent of hydrogen and 2.7 per cent of carbon monoxide contained no hydrogen or carbon monoxide, the oxygen had been entirely consumed, and large percentages of carbon dioxide had been produced. Although these tests showed that bacteria had removed the hydrogen and carbon monoxide, they did not give evidence as to whether the hydrogen and carbon monoxide were removed before the oxygen had been eliminated. This is an important factor because in most mine-fire areas oxygen is always present. The high percentage of carbon dioxide in the final mixtures indicated that at least part of this gas was produced by the solid matter in the liquid.

Effect of Solid Organic Material

Tests were next made in which all solid matter was filtered out and only the liquid was used. They were made to determine whether organic matter, such as decaying wood, and solids were necessary to cause elimination of hydrogen and carbon monoxide. A liter of the decanted liquid was placed in a 19-liter vessel (Figure 2) in contact with a gas mixture made by passing air through incandescent anthracite. About 50 per cent of this gas and 50 per cent of air were introduced into the vessel holding the liquid containing the bacteria. The atmosphere was analyzed periodically to determine the reactivity of the bacteria on the gaseous mixture. The results are summarized in Table I; data are included for a blank test made under similar conditions, except that one part of mercuric chloride was added per 1000 parts of liquid to kill any bacteria present and thus to show whether bacteria caused the reactions.

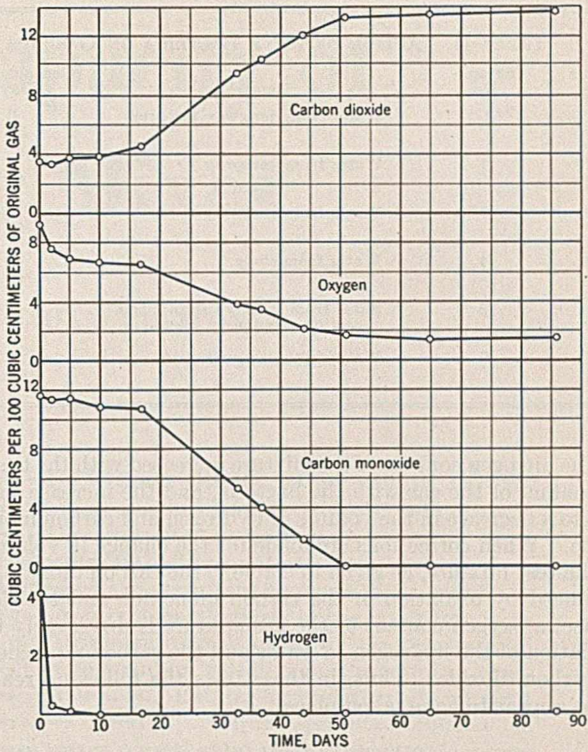


Figure 3. Action of Bacteria on a Gaseous Atmosphere Containing Hydrogen and Carbon Monoxide

Table I. Action of Bacteria on a Gaseous Atmosphere Containing Hydrogen and Carbon Monoxide

Days from Start of Test	Temp., ° C.	Total Pressure, Mm.	Relative Vol.	Gas Analysis, % by Vol.						Calcd. Relative Vol., % by Vol.					
				CO_2	O_2	H_2	CO	CH_4	N_2	CO_2	O_2	H_2	CO	CH_4	N_2
0	23	754	1.000	3.5	9.2	4.1	11.6	0	71.6	3.5	9.2	4.1	11.6	0	71.6
2	24	720	0.952	3.5	8.0	0.3	12.0	0	76.2	3.3	7.6	0.3	11.4	0	72.5
5	22.5	706	0.938	3.9	7.4	0.1	12.2	0	76.4	3.7	6.9	0.1	11.4	0	71.7
10	24	710	0.938	4.1	7.2	0	11.5	0	77.2	3.8	6.7	0	10.8	0	72.4
17	23	705	0.938	4.8	6.9	0	11.4	0	76.9	4.5	6.5	0	10.7	0	72.1
33	24	683	0.898	10.6	4.2	0	5.9	0	79.3	9.5	3.8	0	5.3	0	71.2
37	25	677	0.894	11.7	3.8	0	4.5	0	80.0	10.5	3.4	0	4.0	0	71.5
44	24.5	667	0.879	13.8	2.4	0	2.0	0	81.8	12.1	2.1	0	1.8	0	72.0
51	24	662	0.875	15.2	2.0	0	0	0	82.8	13.3	1.7	0	0	0	72.5
65	25	660	0.879	15.3	1.6	0	0	0	83.1	13.5	1.4	0	0	0	73.0
86	25	675	0.890	15.4	1.7	0	0	0	82.9	13.7	1.5	0	0	0	73.8
Blank Test, Bacteria Killed with $HgCl_2$															
0	27	733	1.000	2.1	11.3	2.0	10.0	0	74.6						
50	25	736	1.010	2.3	11.2	1.8	10.0	0	74.7						

As Table I and Figure 3 show, the hydrogen was completely consumed in 10 days. During the first 17-day period there was little change in the carbon monoxide content. However, after 17 days the elimination of carbon monoxide began, and this gas had disappeared at the end of 51 days. No methane was formed in these tests; therefore the microorganisms causing the elimination of hydrogen and carbon monoxide are not of the same type as those mentioned by Fischer, Lieske, and Winzer (*1*). They found that certain bacteria cause hydrogen and carbon monoxide to combine in the absence of oxygen to form methane:

$$CO + 3H_2 = CH_4 + H_2O$$

They proposed this method for the removal of carbon monoxide from illuminating gas to render the gas nontoxic.

Table II. Action of Mine Bacteria on Gaseous Atmospheres Containing Hydrogen and Carbon Monoxide

Mine No.	Sample No.	Remarks	Contact Time, Days	Compn. of Gas Mixt., % by Vol. CO_2	O_2	H_2	CO	CH_4	N_2
1	1	Water from gangway fire area	0	0.4	11.3	14.3	12.3	0	61.7
			30	7.0	4.7	1.6	7.6	0	79.1
2	2	Water from gangway	0	0.9	9.5	7.8	15.9	0	65.9
			40	5.3	3.3	2.2	13.6	0.3	75.3
2	3	Water from gangway	0	0.9	9.5	7.8	15.9	0	65.9
			40	5.1	2.1	1.0	13.5	0	78.3
2	4	Water from slope	0	0.9	9.5	7.8	15.9	0	65.9
			40	1.6	7.8	5.8	15.8	0.1	68.9
2	5	Slime from inactive abandoned section of mine	0	0.4	11.3	14.3	12.3	0	61.7
			40	0.7	11.1	12.6	10.2	0	65.4
3	6	Water from gangway	0	0.4	11.3	14.3	12.3	0	61.7
			40	7.6	2.6	3.3	9.0	0	77.5

The nitrogen content of the mixture increased with the time of contact of the gas with the bacteria, and the increase was due to a decrease in the volume of hydrogen and carbon monoxide. When corrections are made for the change in volume of the test mixture, as given in Table I, the carbon dioxide is produced by oxidation of the carbon monoxide and the decrease in oxygen content of the gas mixture is due largely to oxidation of the hydrogen to water and the carbon monoxide to carbon dioxide. Thus, in these tests the following reactions appear to have taken place:

$$2H_2 + O_2 = 2H_2O \qquad (1)$$

$$2CO + O_2 = 2CO_2 \qquad (2)$$

The reason for the delayed reaction of the carbon monoxide with oxygen is not clear.

The results show that solid organic matter is not required in the reaction, that hydrogen is more reactive than carbon monoxide in this particular media, that the reaction takes place in atmospheres in which free oxygen is present, and that the reactions are due to living organisms. A control test which was made at the same time and in which mercuric chloride was present showed virtually no change in the composition of the original gas mixture after 50 days of contact.

Bacteria in Water and Slimes

A further step in the investigation was the determination of whether gangway water and slimes from stagnant and other regions in various mines in the anthracite region contained bacteria of a type that would consume carbon monoxide and hydrogen.

Six samples of liquids and slimes were collected from three different mines, and tests were conducted in reaction vessels of the type shown in Figure 1. The results obtained are given in Table II. The samples of water from mines 1 and 3 showed a considerable elimination of hydrogen and carbon monoxide from the gas mixtures after 30 or 40 days of contact with the liquid, while one sample from mine 2 showed practically no change in carbon monoxide concentration after 40 days and the other three only a slight reduction.

Sample 1 was of special significance because it came from the mine-fire area in which the carbon monoxide content of the air had decreased rapidly a few days after the area was sealed. The liquid from the 30-day test was given further treatment in the 19-liter reaction vessel shown in Figure 2. A gas containing hydrogen and carbon monoxide was made by passing air through incandescent anthracite, and a mixture containing about 40 per cent of this gas and 60 per cent of air was prepared. The final mixture contained 9.4 per cent of carbon monoxide (Table III). At the end of 20 days the bacteria had entirely eliminated the carbon monoxide, and only 0.5 per cent of hydrogen remained in the atmosphere. At the end of 40 days the carbon dioxide content had increased slightly and the oxygen content had fallen as shown; however, the major reactions had taken place during the first 20 days. The test was therefore stopped at the end of 60 days. In this test small strips of sponge (*i*, Figure 2), sterilized at 100° C. in an oven for 12 hours, were suspended in the reaction vessel to increase the surface contact between the liquid and the gas. An approximate estimate of the amount of carbon monoxide that was eliminated by the mine water can be obtained from the decrease in carbon monoxide content over the 20-day exposure period and from the volumes of the gas mixture and the mine water containing the bacteria. The data show that for an exposure of 20 days 1 volume of the mine water eliminated approximately 1.7 volumes of carbon monoxide.

Table III. Change in Composition of a Mine-Fire Atmosphere Containing Carbon Monoxide and Hydrogen in Contact with a Gangway Water Containing Bacteria[a]

Days from start of test	0	20	40	60
Carbon dioxide	2.4	12.8	14.5	15.2
Oxygen	11.0	3.7	1.4	0.5
Hydrogen	1.3	0.5	0	0
Carbon monoxide	9.4	0	0	0
Methane	0	0	0	0.1
Nitrogen	75.9	83.0	84.1	84.2

[a] One liter of liquid in contact with 18 liters of gas mixture at start of test.

The rate of elimination of carbon monoxide is ample to account for the elimination of the carbon monoxide in the mine-fire area discussed at the beginning of this report.

These results show conclusively that some waters and sludges in anthracite mines carry unidentified bacteria or microorganisms; under favorable conditions they react rapidly with carbon monoxide to produce carbon dioxide and with hydrogen to produce water vapor, and thus cause the disappearance of these gases in sealed areas.

Acknowledgment

Acknowledgment is made to R. D. Currie, of the Safety Division of the Bureau of Mines, who collected the samples of liquids and slimes reported in Table II.

Literature Cited

(1) Fischer, Franz, Lieske, R., and Winzer, K., *Brennstoff-Chem.*, 11, 452–5 (1930).
(2) Graham, I., *Trans. Inst. Mining Engrs.* (London), 79, 92–111 (1929–30).
(3) Haldane, J. S., and Makgill, R. H., *Ibid.*, 85, 172–85 (1933).

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Whipping Capacity of Ice Cream Mixes

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The improved whipping properties of ice cream mixes brought about by aging can be obtained if butterfat and improvers are absent, but cannot if the mix has not been heated. Higher homogenization pressures favor increased stability and greater maximum overruns without affecting the lie of the overrun-temperature line. Higher homogenization temperatures may accelerate aging effects in mixes where they are normally not apparent.

Butterfat exerts a marked depressing effect upon overruns and determines the level of whip of ice cream mixes. The use of butter in ice cream mixes lowers whipping capacity. This difficulty can be overcome without the use of egg yolk by first reconstituting a cream from butter and using this as normal cream is used in making up the mix. Such mixes whip with abnormal rapidity.

Increased sugar content tends to raise overrun in ice cream mixes, particularly at the lower temperatures; this advantage is offset by the detrimental effect of sugar upon stability and maximum overruns obtainable. Gelatin beyond a certain amount decreases overrun. Sodium alginate stabilizes ice cream mixes remarkably. Carob bean extract acts in much the same way as gelatin but increases the load on the freezer.

PREVIOUS work by the authors,[1] which showed that ice cream overrun is a function of temperature and that this relationship, with certain qualifications, can be shown graphically by a straight line, makes possible the exact comparison of the whipping capacities of different ice cream mixes. Using this graphic method of expressing whipping capacity, the authors studied a number of the factors usually incident to ice cream manufacturing procedure in their effect upon overrun and here present the results of this study.

This report is limited to experiments conducted with batch freezers, but the study is being continued with a freezer of the continuous type. It is believed that a complete investigation of the factors influencing the whipping capacity in the more simple batch freezers is essential as a preliminary to work with continuous freezers since the data thus obtained are of a fundamental character. The work is also limited to mixes of normal composition, reserving for later investigation mixes of extremely high butterfat and solids content, as well as mixes prepared from special ingredients such as frozen cream, powdered milk, and various milk powders low in their lactose content.

It has previously been the custom, in comparing the whipping capacities of ice cream mixes in batch freezers, to record the time interval necessary to obtain a certain overrun. Since this time interval is now known to be dependent upon a number of factors—for instance, the temperature to which the mix is frozen and the speed with which the mix can warm up in the individual freezer, factors that have not been controlled or recorded—satisfactory comparison cannot be made between the data of various investigators.

The authors' previous work[1] showed that, if a number of samples of a given ice cream mix are frozen down to different temperatures and then whipped back, and the overrun data are plotted against temperature, portions of each curve follow along a common straight line. This equilibrium line is the locus of points which represent the highest overruns obtainable with the given mix at the existing temperatures. This line can be used as a measure of the whipping capacity of the mix. In other words, that work showed that if the ice cream mix is whipped long enough for equilibrium to be reached, the resulting overrun for a given mix is dependent upon the temperature, provided that the mix has not been whipped too long. In a brine-cooled 20-quart freezer, equilibrium is attained in about 12 minutes total time in the freezer; in a direct-expansion ammonia freezer with higher dasher speed, the total time is about 8 minutes. If whipping is carried on too long, the mix either warms close to the melting point and the overrun decreases, or an incipient churning of the mix occurs, also with loss of overrun. The data show clearly that, if the freezing process is so adjusted that the temperature corresponding to the desired overrun is reached at the time equilibrium is attained, then the whole process of freezing has been carried out in the shortest possible time. If, as has frequently been the custom in manufacturing procedure, the mix is frozen to lower temperatures than this, then it is necessary to wait for the material to warm up before the desired overrun is attained. On the other hand, if the mix in the freezer is held at higher temperatures than this, the desired overrun can be obtained in less time, but the mix is drawn without the formation of all the ice that can exist at this overrun. Whether or not this causes an impairment of texture has not been determined. Theory clearly indicates that the freezing should be carried out so that equilibrium exists at the time of drawing. Mixes vary considerably in regard to their ability to resist churning. As might be expected, mixes homogenized at the higher pressures are the more stable. It is of considerable interest, too, that mixes of identical composition made up from time to time during the course of nearly two years' work almost always gave identical overrun lines. The whipping capacity of a mix expressed as a function of temperature is therefore a fundamental

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[1] *J. Dairy Sci.*, **20**, 371 (1937).

property of the mix, and, once determined for a certain formula, it can be used as a control for other mixes of the same composition.

Bearing these facts in mind, we shall now discuss the effects on overrun of the various processes and constituents common to ice cream manufacture. In the course of this work the mix was usually prepared, pasteurized, homogenized, and cooled immediately on a surface cooler. One portion of the mix was taken from the cooler and frozen immediately, another portion was frozen after 4 hours, and the rest was frozen after aging for one day at a temperature of 35° F. Only one portion was taken from the cooler because the whipping capacity was usually changing so rapidly at the time that duplicate measurements could not be made. Overruns were recorded every 2 minutes during the freezing process, the recordings usually starting 4 minutes after the mix entered the freezer. Temperatures of the overrun samples were recorded. As shown in the previous report,[1] at equilibrium overrun plots a straight line against temperature. In the graphs presented in this paper this line only will be shown, its upper extremity being the maximum overrun obtained. The line will be referred to in the text as the overrun line and represents the whipping capacity of the mix. The overrun line of aged mixes is usually a plot of the data from three to five separate freezings. The lines representing freezings upon unaged and mixes aged 4 hours are the data from but a single freezing for each separate mix, and the uppermost point is not necessarily the highest overrun that could be attained with these mixes. During most of this work two freezers were used, the overrun line with the direct expansion freezer usually lying slightly above the one obtained with the brine freezer. The data presented are those obtained with the brine freezer.

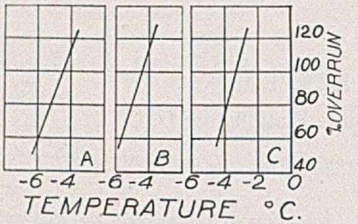

FIGURE 1. OVERRUN LINES OF STANDARD MIXES

A. 8 per cent butterfat
B. 12 per cent butterfat
C. 16 per cent butterfat

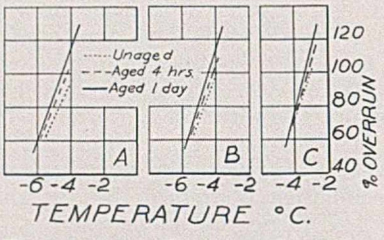

FIGURE 2. OVERRUN LINES OF STANDARD MIXES AFTER DIFFERENT AGING PERIODS

A. 8 per cent butterfat
B. 12 per cent butterfat
C. 16 per cent butterfat

Most of the work reported here has been carried out with three characteristic ice cream mixes. The first contains 8 per cent butterfat, 11 per cent milk-solids-not-fat, and 14 per cent sugar; the second contains 12 per cent butterfat, 10 per cent milk-solids-not-fat, and 14 per cent sugar; the third contains 16 per cent butterfat, 8 per cent milk-solids-not-fat, and 14 per cent sugar. Figure 1 shows the overrun lines for these mixes when made up without gelatin, homogenized at 2500 pounds per square inch pressure, and aged one day. These overrun lines are taken as the standard for comparison in presenting the data of this report.

Aging

Although comparison of aged and unaged mixes will be made throughout the report, a brief discussion of the effects of aging upon overrun is perhaps not out of place here. An unaged mix is usually less stable to the action of the beaters, possesses lower whipping capacity, and cannot be whipped to as high a maximum overrun as a mix that is aged one day. In respect to these properties, a 4-hour-aged mix may approach the day-old mix closely, but more often it is intermediate between the fresh and the day-old mix.

The improved whipping properties of a mix can be obtained through aging even if no improver is present and also if butterfat is absent. They cannot be obtained unless the mix has been heated as in the pasteurization process. It seems evident, then, that the effects of aging concern the serum solids and are the result of the heating process. The stability of mixes to the action of the beaters also increases with aging when butterfat is present. This effect is concerned primarily with the condition of the butterfat and may be the result in part simply of the solidification of the fat particle.

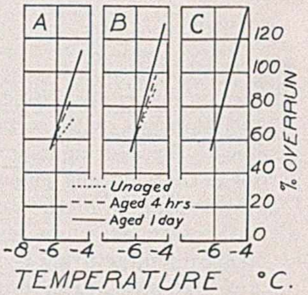

FIGURE 3. EFFECT OF HOMOGENIZATION ON WHIPPING CAPACITY

A. 1500 pounds per square inch
B. 2500 pounds per square inch
C. 3500 pounds per square inch

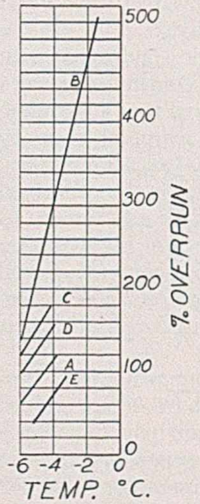

FIGURE 4. EFFECT OF BUTTERFAT ON WHIPPING CAPACITY

A. 12 per cent butterfat
B. No butterfat
C. 0.5 per cent butterfat
D. 1.0 per cent butterfat
E. Butter as fat source, 12 per cent butterfat

As will be evident from data to be presented subsequently, excess gelatin or other stabilizer may cause a decrease in whipping capacity upon aging. This is invariably caused by heavy gelation. Figure 2 gives overrun lines for aged and unaged standard mixes.

Homogenization Temperature and Pressure

Increases in homogenization pressure above 1500 pounds per square inch do not alter the position of the mix temperature–overrun equilibrium line but do increase markedly its stability to the action of the beaters as well as the maximum overruns obtainable in both the aged and the unaged mixes. For example, Figure 3 gives the overrun lines of three normal 12 per cent butterfat mixes made up at different times and homogenized at different pressures. The lie of the overrun lines is the same for the three mixes, but stability and maximum overrun are raised by increasing the homogenization pressure. Similar relationships were found to exist with the mixes containing 8 and 12 per cent butterfat.

An increase of homogenization temperature may increase whipping capacity of certain high-fat mixes. As will be shown, the process of aging seems to receive an impetus. In mixes of high gelatin content higher temperatures of homogenization may decrease whipping capacity, probably because of accelerated gelatin. Bearing these facts in mind, we can now consider the effects of ice cream constituents upon whipping capacity.

Butterfat

A mixture of sugar and milk-solids-not-fat of the water concentration normally used in ice cream mixes whips readily upon freezing. It is known that overrun is decreased by the addition of butterfat. The exact magnitude of this decrease had not previously been measured. Figure 4 shows the overrun lines of a mix containing different amounts of butterfat.

The nature of the surface of the fat particle is probably also of importance in its effect upon overrun. Line *E* (Figure 4) represents the same mix containing 12 per cent butterfat, but in this case butter was used as the source of milk fat. This overrun line lies markedly below the others, which indicates that the surface of the fat particle is important.

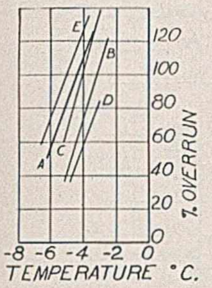

FIGURE 5. EFFECT OF THE BUTTERFAT SURFACE ON WHIPPING CAPACITY

- *A.* Mix made from normal cream and also from butter cream
- *B.* Mix made from butter
- *C.* Butter mix with egg yolk added
- *D.* Butter mix from butter cream made with concentrated skim milk
- *E.* Butter mix made from butter cream from dilute skim milk

Butter

Butter has long been used as an emergency source of fat in ice cream manufacture; one drawback is the poor whipping quality of mixes in which it is used. This has been overcome in part by the addition of egg yolk. *A* (Figure 5) is the overrun line of the normal mix made from cream; *B* represents the same mix in which the butterfat was supplied by butter. *C* is the same butter mix with egg yolk added. In the preparation of these mixes the butter was simply melted in the pasteurization kettle and homogenized with the mix.

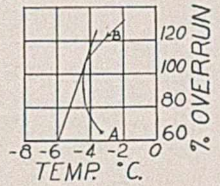

FIGURE 6. COMPARATIVE RATE OF WHIPPING OF MIXES MADE FROM NORMAL CREAM (*A*), BUTTER CREAM (*B*)

There seemed to be the possibility that the surface of the butter particle might be coated so heavily with protein as to mask the effect of the butter particle. In order to prove this point, butter was melted and homogenized with the condensed skim milk (approximately 35 per cent total solids) that was to be used. This cream was then used in making up the mix, and the whole mass was homogenized as if fresh cream were being employed. The overruns from this mix (Figure 5, *D*) were markedly lower than those obtained when plain butter was used.

The butter was then homogenized in skim milk, and this cream was used in the preparation of the mix; the normal overrun was obtained (Figure 5, *A*). If the butter was made into a cream diluted with skim milk, overruns were greater than normal (Figure 5, *E*). It would seem, therefore, that the difficulties of low overrun encountered when butter is the source of milk fat in ice cream may be overcome by the simple expedient of preparing a cream of skim milk and butterfat by homogenization and using this cream as normal cream is used in the preparation of the mix.

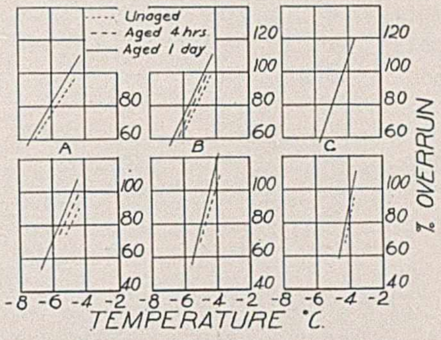

FIGURE 7. WHIPPING CAPACITIES OF MIXES CONTAINING (*above*) 16 PER CENT CANE SUGAR AND (*below*) 16 PER CENT SUGAR OF WHICH 4 PER CENT IS DEXTROSE

- *A.* 8 per cent butterfat
- *B.* 12 per cent butterfat
- *C.* 16 per cent butterfat

Another observation of interest is the speed with which these mixes made from butter cream whipped. No mixes other than these have been encountered in nearly two years' work in which temperature-overrun equilibrium was reached in the brine freezer in less than 10 to 12 minutes total time in the freezer. As Figure 6 shows, the equilibrium curve is approached from below in the case of the normal mix. The butter mix whips so rapidly, however, that equilibrium is approached from above. Equilibrium was reached with the butter mix in 6 minutes, with the cream mix in 12 minutes. The butter mix could have been drawn from the freezer completely frozen and whipped in 6 minutes. Two facts have therefore been demonstrated: (1) The whipping capacity of a mix can be varied by the simple expedient of varying the fat particle, and (2) the speed of whipping can be altered by the same process. This presents opportunity for further work which should be of considerable value.

Sugar

In spite of the fact that sugar has long been known as an overrun deterrent, we should expect that sugar, by lowering the freezing point of a mix, would cause higher overruns at given temperatures. Figure 7 shows that the stability of mixes and maximum overruns are lowered with increase in sugar content; at lower temperatures, particularly with mixes containing corn sugar, there is a marked increase in the overruns under equilibrium conditions over the corresponding 14 per cent sugar content mixes. If cane sugar in increasing amounts is substituted for the corn sugar until mixes of the same freezing points are obtained, the overrun curves are practically identical with the lines of the corn sugar mixes; thus the effect is largely the result of lowering the freezing point. It is known that creams containing sugar churn more readily. It is likely that the instability of ice cream mixes high in sugar content is the result of this action of sugar in accelerating churning.

Stabilizers

Of the so-called stabilizers, gelatin is one of the most commonly used. In proper amounts it favors the formation

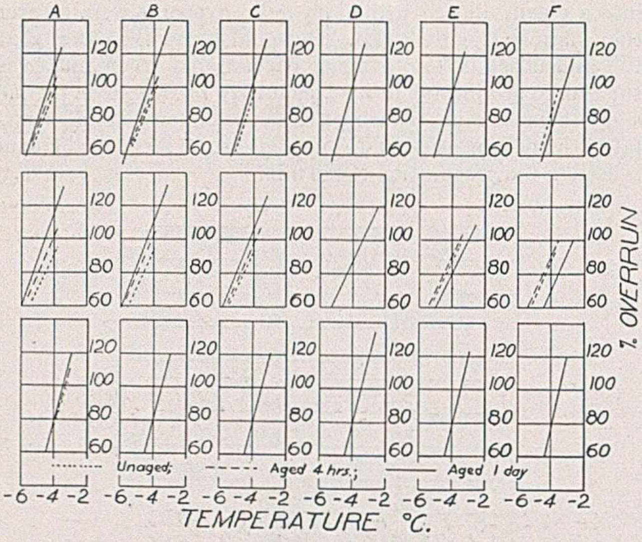

FIGURE 8. EFFECT OF GELATIN UPON WHIPPING CAPACITY OF MIXES CONTAINING (*above*) 8 PER CENT, (*center*) 12 PER CENT, AND (*below*) 16 PER CENT BUTTERFAT

A. No gelatin
B. 0.1 per cent gelatin
C. 0.2 per cent gelatin
D. 0.3 per cent gelatin
E. 0.4 per cent gelatin
F. 0.5 per cent gelatin

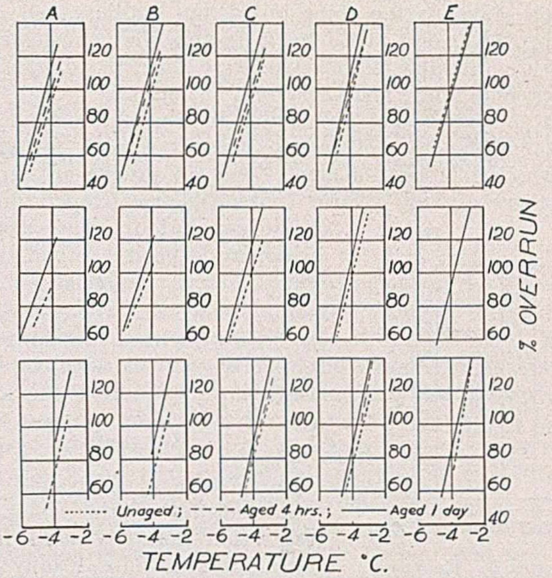

FIGURE 10. EFFECT OF SODIUM ALGINATE UPON THE WHIPPING CAPACITY OF MIXES CONTAINING (*above*) 8 PER CENT (*center*) 12 PER CENT, AND (*below*) 16 PER CENT BUTTERFAT

A. No sodium alginate
B. 0.1 per cent sodium alginate
C. 0.2 per cent sodium alginate
D. 0.3 per cent sodium alginate
E. 0.4 per cent sodium alginate

of small ice crystals and increases the melting resistance without the formation of a mass that will not melt. As Figure 8 shows, an increase in the amount of gelatin decreases the whipping capacity of 8 per cent butterfat mixes. This effect is not as marked with 12 per cent butterfat mixes and is entirely absent in the mixes containing 16 per cent butterfat (Figure 8). In comparing these curves later with the data on sodium alginate, it must be remembered that the lines for unaged and 4-hour aged mixes are those of single freezings and that the highest overruns recorded are not necessarily the highest that could be obtained. The solid line indicating the whipping capacity of aged mixes is the composite of from three to five freezings, and its uppermost point indicates the highest overrun obtainable.

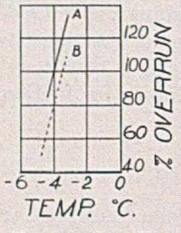

FIGURE 9. EFFECT OF HIGH-TEMPERATURE HOMOGENIZATION ON THE AGING OF 16 PER CENT BUTTERFAT MIXES

A. Unaged and low-temperature frozen-aged
B. Higher temperature aged

At a later date it was found that aging effects could be produced in the high-butterfat mixes by homogenization at higher temperatures. This will be referred to again in the experiments with sodium alginate but is illustrated in Figure 9. The solid line of the aged mix is realized only if the mix is frozen at a comparatively high temperature. Otherwise the lower overrun line results. The mix thus has two equilibrium lines.

Sodium alginate in a form especially prepared for the purpose is another stabilizer recommended for ice cream. The claim is made that with its use aging is unnecessary. Actually, aging does improve the whipping properties of the mixes containing sodium alginate. However, sodium alginate does have the remarkable property of immediately stabilizing the butterfat to the action of the beaters so that freshly prepared mixes can easily be brought to the desired overruns. It is thus a double stabilizer; it stabilizes the structure (as does gelatin) and the particles in addition. These effects are shown in Figure 10 for the mixes of varying butterfat content. Of particular interest are the high overruns obtainable under certain conditions with both unaged and aged mixes.

As mentioned previously, the aging effects produced in the 16 per cent fat content mixes were found to be caused by the high temperature of pasteurization and homogenization (71° C.) recommended for use when sodium alginate is employed, rather than to any specific effect of the alginate.

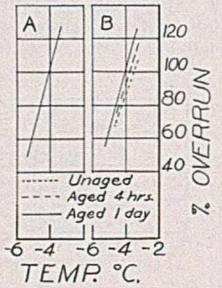

FIGURE 11. WHIPPING CAPACITY OF A 12% BUTTERFAT MIX CONTAINING CAROB BEAN EXTRACT COMPARED WITH A SIMILAR MIX CONTAINING GELATIN

A. Gelatin 0.3 per cent
B. Carob bean extract, 0.2 per cent

A few experiments were carried out to study the use of a certain carob bean extract, as an improver in ice cream. This material acts in many respects as does gelatin. Its effect upon whipping and aging is shown in Figure 11. In spite of the fact that the overrun of these mixes is similar to the overrun of gelatin mixes, the presence of this product was shown to increase markedly the load on the freezer. Where the gelatin mix of the same composition would cause the motor to draw 6 amperes at a given temperature, the mix containing the extract would draw 7 amperes at the same point.

Discussion

In the foregoing a survey has been made of factors influencing the overrun of ice cream mixes. It is noteworthy that 100 per cent overrun, the highest usually considered desirable to take, can be obtained with practically all of the mixes used and reported here. It is a matter of so adjusting the freezing process that the required temperature is reached in the freezer within the necessary time interval before incipient churning starts. The realization of this fact should do much to clarify the confusion that exists concerning the comparative whipping properties of various mixes and the procedure that must be followed to obtain the higher overruns.

Since the work here reported was concerned primarily with overrun, no reference has heretofore been made to ice cream quality. Other things being equal, the ice cream that can be drawn from the freezer with the greatest amount of water in the form of ice has the best texture because the ice crystals will not grow so much in the hardening room. (This is probably the reason ice creams made from aged mixes are superior.) Therefore, those mixes that can be drawn from the freezer at the desired overrun with the greatest amount of water in the form of ice present are to be preferred. Moreover, ice cream should be drawn from the freezer while the temperature-overrun equilibrium exists, because at this point the greatest amount of water possible at the chosen overrun has been frozen to ice and the best possible texture is therefore to be had.

Enthalpy-Concentration Charts from Vapor Pressure Data

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THE minimum thermal data required for the construction of an enthalpy-concentration chart for a liquid solution are the heats of dilution at one temperature, and heat capacities over the entire temperature and concentration range to be covered; or else, heat capacities at one concentration, and heats of dilution over the entire temperature and concentration range (*6*). Experimental data on either heat capacities or heats of dilution at higher concentrations and temperatures are scarce; consequently enthalpy-concentration charts have been prepared for only few systems. However, information is available on the equilibrium properties (notably vapor pressures) of many liquid solutions, from which heats of dilution at higher concentrations and temperatures can be calculated. The enthalpy-concentration chart for the system can then be constructed by combining the calculated heats of dilution with experimental heat capacities at low concentrations. The relations involved in one of the several possible conversions of this nature are derived and illustrated here.

The experimental data required for the construction of an enthalpy-concentration chart by the method under consideration are (*a*) heat capacities of the solution at any one concentration, over the entire temperature range and (*b*) vapor pressures of the solution over the concentration and temperature range to be covered. The method is applicable to all systems containing a single volatile constituent. The accuracy of the calculated values is discussed at the end of the paper.

All methods based on pure thermodynamics for the calculation of thermal properties from equilibrium properties include the differentiation of the equilibrium data. The differentiation can be greatly simplified if the equilibrium data can be converted to a linear or nearly linear form. The most convenient of the several possible "linear" relations for the present purpose is the Dühring plot, since it has to be constructed anyway for calculations on most processes involving solutions.

Brown (*3*) showed how the Clapeyron relations for a liquid and for a solution containing that liquid as solvent can be combined to give a relation in which the differential term is the slope of the Dühring line. The slopes of the Dühring lines are, by all present evidence, constant at low concentrations and vary only slightly at higher concentrations. The relation is:

$$\frac{dt'}{dt} = \frac{\Delta H \, \Delta V' T'}{\Delta H' \, \Delta V \, T} = D \qquad (1)$$

where at a given concentration,

t' = saturation temp. of solution at pressure P, ° C. or ° F.
T' = saturation temp. of solution at pressure P, ° K or ° R.
t = saturation temp. of solvent at pressure P, ° C. or ° F.
T = saturation temp. of solvent at pressure P, ° K or ° R.
D = slope of Dühring line
ΔH = latent heat of solvent at temp. t and pressure P
$\Delta H'$ = latent heat of solvent in solution at temp. t' and pressure P
ΔV = difference between gas and liquid volumes of solvent at temp. t and pressure P
$\Delta V'$ = difference between gas and liquid volumes of solvent at temp. t' and pressure P

This is an exact relation, applicable to all systems containing a single volatile constituent. To simplify future discussion, it will be assumed that the volatile constituent is water, and English units will be used. This will make all quantities in Equation 1 and future equations, steam table quantities.

Equation 1 can be simplified, without introducing a serious error, by neglecting the volume of the liquid phase. Then $\Delta V = V_{\text{gas}}$, denoted by V hereafter. Furthermore, for ideal gases at the same pressure,

$$\frac{T'V'}{T\,V} = \left(\frac{T'}{T}\right)^2$$

If ϕ, a measure of deviation from the ideal gas law, is defined as

$$\phi = \frac{T'V'}{T\,V} - \left(\frac{T'}{T}\right)^2 \qquad (2)$$

Equation 1 can be thrown into a convenient form for calculations:

$$\Delta H' = \frac{\Delta H}{D}\left[\left(\frac{T'}{T}\right)^2 + \phi\right] \qquad (3)$$

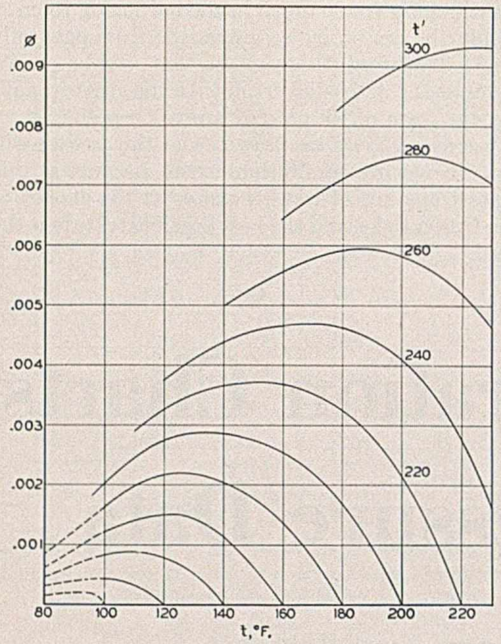

FIGURE 1. ϕ *vs.* t FOR STEAM AT CONSTANT SUPERHEAT TEMPERATURES

Figure 1, based on Keenan's steam tables (*5*), gives values of ϕ *vs.* t for steam, for boiling point elevations up to 100° F. For values of t below 100° F., ϕ can safely be neglected.

$\Delta H'$ has been defined as the latent heat of water in the solution. It is therefore the difference between the heat contents of water in the vapor and the liquid state:

$$\Delta H' = H_v - \overline{H}_1$$

or

$$\overline{H}_1 = H_v - \Delta H' \quad (4)$$

where $\overline{H}_1$ = partial heat content of water in solution, B. t. u./lb. water

H_v = heat content of steam at temp. t' and pressure P, B. t. u./lb. steam

The heat quantity appearing on the enthalpy-concentration chart is the relative enthalpy of the solution, H, in B. t. u. per pound of solution, plotted as isotherms *vs.* concentration. H is referred to arbitrarily chosen conditions of the solvent and the solute. At any given temperature, t', the relative enthalpy of a solution of concentration W_b pounds of solute per pound of solution can be calculated by

$$H_b = \frac{H_a - \int_{W_a}^{W_b} \overline{H}_1 \, d\left(1 - \frac{W_a}{W}\right)}{W_a/W_b} \quad (5)$$

where H_a = relative enthalpy of solution at temp. t' and concentration W_a, B. t. u./lb. of solution

H_b = relative enthalpy of solution at temp. t' and concentration W_b, B. t. u./lb. of solution

Equation 5 can be derived as follows: Consider the isothermal evaporation of water from one pound of dilute solution. Let W be the number of pounds of solute per pound of solution; consider the initial concentration as W_a. If X pounds of water are removed, the final concentration is:

$$W_b = W_a/(1 - X) \quad (6)$$

From this, the water removed is:

$$X = 1 - W_a/W_b \quad (7)$$

Writing a material balance,

$$1 = W_a/W_b + (1 - W_a/W_b) \quad (8)$$

The heat balance is:

$$H_a + \int_{W_a}^{W_b} \Delta H' d(1 - W_a/W) = (W_a/W_b)H_b + \int_{W_a}^{W_b} H_v d(1 - W_a/W) \quad (9)$$

$\int \Delta H' d(1 - W_a/W)$ is the heat input into the solution, where $\Delta H'$ is the latent heat at any concentration, and $d(1 - W_a/W)$ is the number of pounds of water removed at that concentration.

Noting that $H_v - \Delta H' = \overline{H}_1$ (Equation 4) and solving for H_b, we obtain Equation 5.

The value of the relative enthalpy, H_a, at concentration W_a and temperature t', may be assumed to be zero—that is, the datum from which all other enthalpies are calculated. Since the precision in determining relative enthalpies at low concentration may be poor by this method, experimental heats of dilution at low concentrations should be available if it is desired to refer the enthalpies to the customary standard state of infinite dilution at some chosen temperature.

When the relative enthalpy at a given temperature and concentration is known, the relative enthalpy at the same concentration but a different temperature may be calculated by means of the Person-Kirchoff law:

$$dH = C_p dt \quad (10)$$

where C_p = heat capacity of solution at constant pressure

Application

The application of Equations 3, 4, 5, and 10 to the calculation of the 120° F. isotherm on the enthalpy-concentration chart for sodium hydroxide solutions is shown in the example

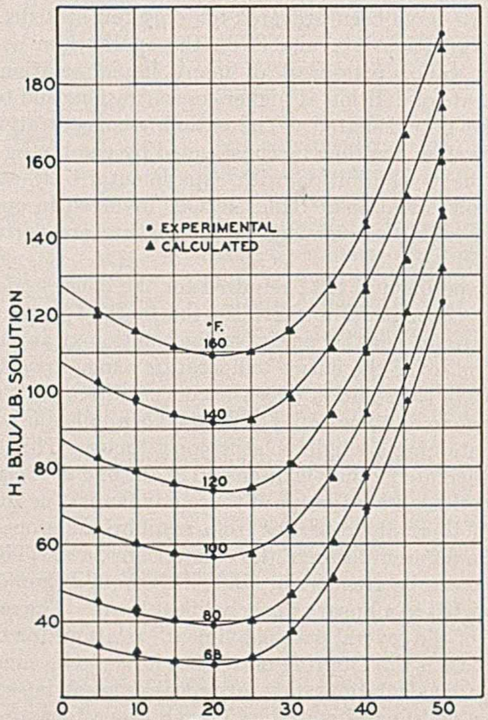

FIGURE 2. ENTHALPY-CONCENTRATION CHART FOR SODIUM HYDROXIDE SOLUTIONS

Reference conditions: liquid water at 32 ° F. for the solvent, infinite dilution at 68 ° F. for the solute which follows. Other isotherms are calculated in an identical manner. The enthalpy-concentration chart (Figure 2) shows a comparison for values of H to 50 per cent by weight sodium hydroxide and 160° F. between the calculated values and experimental values referred to later.

CONSTRUCTION OF DÜHRING PLOT. Complete data on the vapor pressures of sodium hydroxide solutions, as determined by various investigators, are available up to about 60 per cent by weight from 32° to 212° F. (*4*). A convenient correlation of the original data is a plot of $(t' - t)$ isotherms *vs.* concentration (Figure 3). The smoothed values of $(t' - t)$ can be transferred directly to the Dühring plot (Figure 4). The heavy line shows the position of the same value of $(t' - t)$ on the two plots. The correlation should be based on the original data and done with great care. It will be shown later to what extent errors in the Dühring plot affect the calculated values of H.

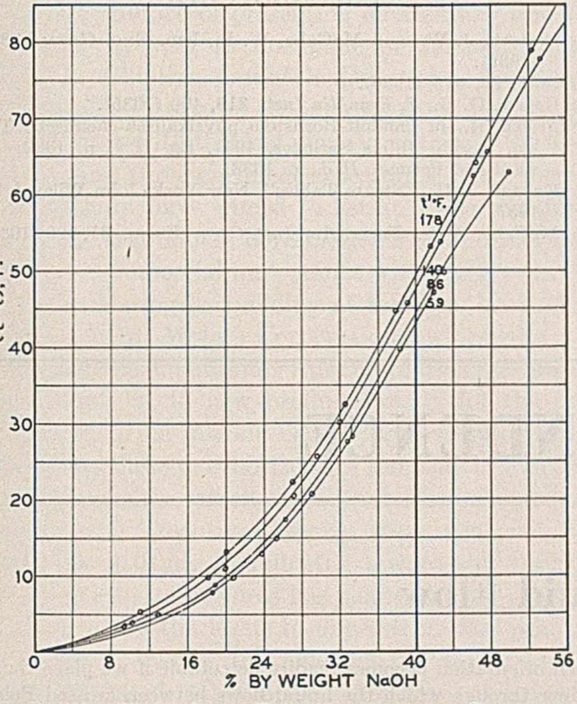

FIGURE 3. $(t' - t)$ *vs.* CONCENTRATION AT CONSTANT BOILING TEMPERATURES FOR SODIUM HYDROXIDE SOLUTIONS

CALCULATION of $\overline{H}_1$. For the construction of an isotherm on the enthalpy-concentration chart, values of $\overline{H}_1$ at one temperature and over the contemplated concentration range are required. Equations 3 and 4 are used for the calculation of $\overline{H}_1$. Values of t at various concentrations corresponding to $t' = 120$ are read from the Dühring plot. The Dühring plot should be large enough so that values of t can be read within 0.1° F.

The Dühring lines on Figure 4 are indicated as being straight at all concentrations. This is undoubtedly incorrect above 30 per cent concentration, but the available data are not exact enough to establish the curvature of the lines. The extent of error introduced by assuming straight lines shows up in the divergence between observed and calculated values at higher concentrations in Figure 2.

Values of ΔH, the latent heat of water at saturation temperature t, and H_v, the heat content of superheated steam at 120° F. and the pressure corresponding to saturation temperature t of water, were read from plots based on the Keenan steam tables (*5*). Values of the correction, ϕ, are read from Figure 1 at the 120° F. isotherm and the various values of t.

The following table summarizes the calculation of $\overline{H}_1$ at 120° F. for two concentrations (from Equations 3 and 4):

	% NaOH by Weight			% NaOH by Weight	
	30	50		30	50
D	1.0490	1.1068	$(T'/T)^2 + \phi$	1.0922	1.2799
t, ° F.	95.09	52.77	ΔH	1039.0	1062.2
T, ° R.	554.78	512.46	$\Delta H'$	1081.8	1228.3
$(T'/T)^2$	1.0918	1.2796	H_v	1113.3	1114.1
ϕ	0.0004	0.0003	$\overline{H}_1$	+31.5	−114.2

CONSTRUCTION OF ENTHALPY-CONCENTRATION CHART. Pure water at 68° F. was chosen as reference condition for the solute, since reliable experimental heats of dilution down to infinite dilution are available at that temperature. The reference condition of the solvent is that of the steam tables—namely, liquid water at 32° F. As a basis in the application of Equation 5, the relative enthalpy, H_a, is assumed to be that of a solution of concentration 20 per cent by weight sodium hydroxide at 120° F. This value for H_a—namely, 73.9 B. t. u. per pound of solution—was obtained by application of Equation 10 to experimental data on heats of dilution (*1*) between 20 per cent by weight sodium hydroxide and infinite dilution, and experimental heat capacities (*2*) at the same concentration.

The following table shows the steps required in the calculation of H. The last column gives Bertetti and McCabe's experimental values for H, referred to the same conditions as the calculated values.

W_b	$\frac{W_a}{W_b}$	$1 - \frac{W_a}{W_b}$	$\overline{H}_1$	$\int_{W_a}^{W_b} \overline{H}_1 d\left(1 - \frac{W_a}{W}\right)$	$H_{\text{calcd.}}$	$H_{\text{exptl.}}$
0.2	1	0	+76.0	0	73.9	73.9
0.3	0.667	0.333	+31.5	+20.2	80.5	80.7
0.4	0.500	0.500	−62.0	+19.0	109.8	110.1
0.5	0.400	0.600	−114.2	+10.0	159.7	162.3

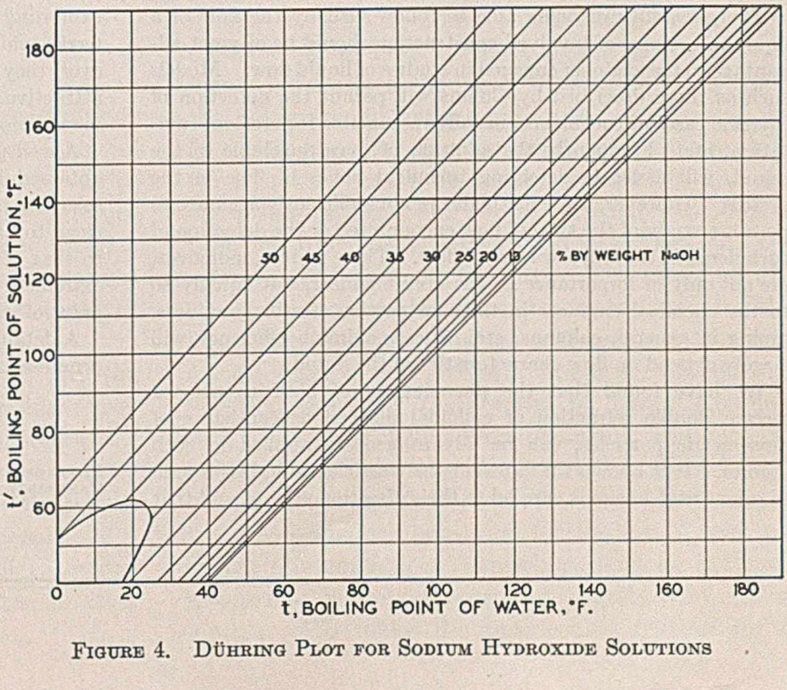

FIGURE 4. DÜHRING PLOT FOR SODIUM HYDROXIDE SOLUTIONS

Accuracy

The chief source of errors in this method lies in the determination of the Dühring line slopes. The order of magnitude of ΔH for steam is 1000 B. t. u. From Equation 3 an error of one thousandth in D will introduce an error of about 1 B. t. u. in $\Delta H'$. This error will be numerically transferred to $\overline{H}_1$. The resultant error in H, the relative enthalpy, is a function of the concentration at which the error occurs. From Equation 5, for an average error of E B. t. u. in $\Delta H'$ between concentrations W_a and W_b, the error in H is:

$$\frac{H_a - \int_{W_a}^{W_b} (\overline{H}_1 + E)d\left(1 - \frac{W_a}{W}\right)}{W_a/W_b} - \frac{H_a - \int_{W_a}^{W_b} \overline{H}_1 d\left(1 - \frac{W_a}{W}\right)}{W_a/W_b} \qquad (11)$$

or $E\,(1 - W_b/W_a)$ B. t. u.

The following table shows the order of magnitude of errors in H due to errors of one thousandth and one hundredth in D over a 10 per cent concentration range:

		Error in H, B. t. u.	
W_a	W_b	0.001 error in D	0.01 error in D
0.1	0.2	1.0	10
0.2	0.3	0.50	5.0
0.3	0.4	0.33	3.3
0.4	0.5	0.25	2.5

These errors become cumulative as Equation 5 is integrated from low to high concentration. This, combined with the fact that vapor pressure data are likely to be less reliable at high than at low concentrations, will tend to give larger errors at higher concentrations.

Literature Cited

(1) Bertetti, J. W., and McCabe, W. L., Ind. Eng. Chem., **28**, 247 (1936).
(2) *Ibid.*, **28**, 375 (1936).
(3) Brown, G. G., *J. Franklin Inst.*, **219**, 406 (1935).
(4) Fricke, R., in Landolt-Börnstein physikalisch-chemische Tabellen, Berlin, Julius Springer, 1931, Eg. II b, p. 1332; Hayward and Perman, *Ibid.*, p. 1333.
(5) Keenan, J. H., "Steam Tables", New York, John Wiley & Sons, 1937.
(6) McCabe, W. L., *Trans. Am. Inst. Chem Engrs.*, **31**, 129 (1934).

CORRESPONDENCE

Study of Liquid Flow

Sir: In *The Du Pont Magazine* [**33**, No. 3, 3 *et seq.* (1939)] we find an article by W. T. Collins "Research Employs Plastics." This publication is primarily devoted to a discussion of the outstanding advantages to be gained by the use of transparent plastics—for example, "Pyralin"—in the construction of models for hydraulic research work.

The possibility of being able to follow visually the flow of a liquid in systems of involved construction should be of great advantage to the engineer engaged in studies of liquid flow. Models such as those described by Collins will permit the detection of extreme cases of turbulence, usually responsible for erosion, cavitation, etc. Frequently the addition of dyes, insoluble in the liquid, will assist in detecting turbulent zones of flow in the system. However, these methods are not sufficiently accurate to permit a study of the type of flow encountered or the detection of turbulence in cases of low rates of flow. These factors, moreover, are not only of importance to the civil engineer, but equally so to the chemical engineer in the construction of stills, rectifiers, piping in general, columns, etc., since maximum efficiency will largely depend on flow characteristics of the liquid.

We have found that the phenomenon of birefringence, or stream double refraction of colloidal dispersions consisting of anisometric particles, can be advantageously applied in such studies. It is known that anisometric particles will always tend to orient with one axis parallel to their direction of flow, and that such orientation becomes readily detectable if we place the container through which the liquid flows between crossed Polaroid films or plates and illuminate it with a strong source of diffuse light.

Highly diluted water dispersions of natural bentonite have proved especially suited for such work. Other colloidal sols exhibiting stream double refraction—i. e., vanadium pentoxide, ferric oxide, soap solutions, etc.—have also been tested. However, they have certain disadvantages which make their use less attractive. The most important are color, change of the surface tension of the liquid, difficulty of production, and cost.

A well prepared one per cent dispersion of bentonite in water obtained by fractionating bentonite in a supercentrifuge and selecting fractions with particles below 50 mμ will be practically clear to the eye, have a viscosity and a surface tension close to that of water, and exhibit pronounced birefringence even at extremely low rates of flow for temperatures up to the boiling point of water.

A detailed study of liquid flow under different conditions is in progress and will be published later.

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