Butanol and Acetone from Corn[1]

A Description of the Fermentation Process

By D. H. Killeffer, Associate Editor

The low price of butanol and the high solvent efficiency of butyl acetate are fundamental to the thriving industry of modern nitrocellulose lacquers. The manufacture of this material by the fermentation of cornstarch is described in this article and the economic effect of the by-products of this process are discussed.

A MUSHROOM as tall and as sturdy as an oak, or an oak as swift to grow as a mushroom, should be classed among the botanists' improbabilities, but nothing short of this could be fairly compared to the rapid growth and sound permanence of chemical industry in America. Unit after unit, based upon some strange habit of matter newly discovered or given new importance by changing circumstances, has developed almost overnight into a profitable part of this young and growing industry. Circumstances have played an important role in this succession of wonders, and persevering research has furnished the *elixir vitae* to keep it going. Few better illustrations of this exist than in the development, by careful research, of the American butanol industry on slender threads of circumstance connecting the British War Office, an odd microörganism, a potential swimming pool filled with an undesired by-product, an early unsuccessful effort at rubber synthesis, the demise of the American whisky industry, the unavoidable limitation of the wood distillation industry, a new type of nitrated cotton, the manufacture of paint and varnish, and the American corn crop.

Early History

To bring these apparently isolated circumstances into their proper mutual relations, it is necessary to go back to 1910, and before, when energetic efforts were being made to synthesize rubber. Polymerizations of butadiene and of isoprene were the bases of hope for the solution of this problem but, unfortunately, neither of these raw materials was to be had easily. At this point a microörganism, *clostridium acetobutylicum* (*Weizmann*) to be accurate, was found to possess a remarkable appetite for starch and a still more remarkable ability to convert it into acetone and butanol. The butanol might well serve as a raw material for the preparation of both butadiene and isoprene. Thus the growth process of the microbe was carefully studied, without, be it noted, any great advantage to the still non-existent industry of rubber synthesis. The second circumstantial thread begins with a peculiar specification of the British War Office that smokeless powder for the British armies be made with acetone as a component of the colloiding solvent, and leads to the beginning of the World War when quantities of powder were required so unimaginably huge that the wood distillers could not be expected to make enough acetone to produce it. In this emergency, the war office dug up the rubber synthesists' microbe and put it to work in England, India, and Canada, changing starch into acetone, to make up the deficit, and butanol. Later, after our entrance into the conflict, an erstwhile whisky distillery in the Indiana corn belt was converted into a plant for the manufacture of acetone under the joint control of the American and British Governments. This story properly begins with this converted distillery, for it has served as the foundation on which a new American industry has been built.

Economic Utilization

The action of the *clostridium* in this old distillery produced great quantities of acetone, which was in urgent demand during the war as a solvent for nitrocellulose, the latter being made into smokeless powder for the British and airplane dope for the Americans. The disguised blessing in this operation was that every pound of acetone produced was accompanied by two of butanol, and although everyone wanted acetone no one was at all interested in butanol. Some of this very plentiful by-product, it is true, was laboriously converted into methylethyl ketone (butanol-1 ⟶ butylene ⟶ butanol-2 ⟶ methylethyl ketone), which was utilized by being added to the acetone output with some of the ethanol simultaneously produced during the fermentation. No one could be persuaded to show interest in the vast amounts of butanol left unused by this operation and immense vats—one now serves very satisfactorily as a swimming pool—were built to conserve it in the hope that it might later find profitable use. It is fortunate that this bit of economy was practiced, despite the expense attached to building the vats, for this surplus butanol now shares equally with "low viscosity cotton" the honors for the founding of our lusty young industry of nitrocellulose lacquers. It is somewhat doubtful if this would have been the case had capital been required to go into its manufacture without the benefit of the compelling proof of its fitness which this surplus furnished.

The swimming pool full of butanol became immediately important upon the discovery of a method of making nitrated cotton of much lower viscosity in solution than the ordinary, for it made readily available an excellent solvent, butyl acetate, at relatively low cost. These two things, cheap butanol and low viscosity cotton, are the foundation of the lacquer industry whose phenomenal growth is among the most amazing of modern industrial wonders. Little more than three years ago nitrocellulose lacquers had been used only in small quantities as a protection for metal surfaces and for airplane wings, whereas today the department stores offer a dozen different varieties in dozens of colors and shades for household use and there are few automobiles made whose finish is not a lacquer. The quantities of lacquer used are increasing at a prodigious rate and, concurrently, the output of butanol has had to grow to supply the necessary solvent. Within the past twelve months the butanol output has been more than doubled, and a still further increase of an approximately equal amount is expected within another year.

The effect of the lacquer made from butanol on the paint and varnish industry has been serious but the wood distillers, already under an accumulation of difficulties, have found it hard to survive the manufacture and sale of the huge quantities of acetone produced as a by-product of this operation. The activities of the microbe result in the production of butanol, acetone, and ethanol in the ratio of 6:3:1, and thus the present unavoidable output of acetone amounts to some 30 tons per day. This must be absorbed by industry, and since no corresponding increase in use has been developed it has operated to control acetone prices. The wood distillers find their domestic market seriously limited by this and their export market, with the exception of Great Britain, practically wiped out. It is interesting to note that this exception comes about because of the British Safeguarding of Industries Act, which provides that acetone made by fermentation shall pay

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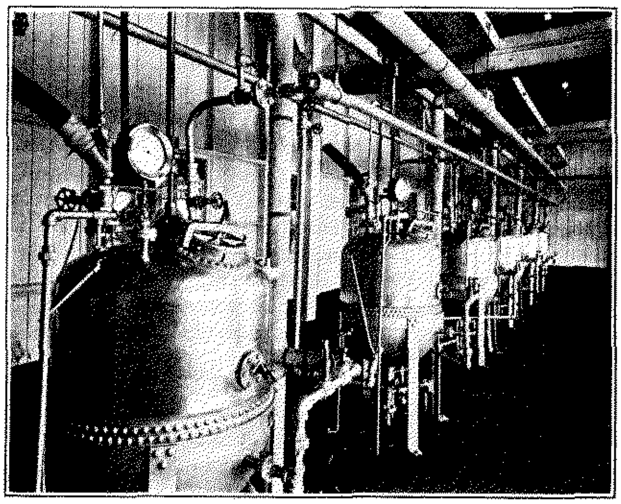
a duty of 33 per cent, whereas that from wood distillation pays only 17 per cent.

The shift of emphasis from butanol, desired by the rubber synthesists, to acetone, important during the war, and now back to butanol, a fundamental raw material for a new and very important industry, is characteristic of the kaleidoscopic changes constantly occurring in the rapid development of chemical industry. A useless by-product, expensive to dispose of today, often becomes overnight the valuable part of one's output. The changing face of affairs under such circumstances can only be met by continuous, energetic research. New ideas come so rapidly to an intensively thoughtful industry that no one can afford to be lulled into fancied security by things as they are, for they have an altogether too disconcerting way of changing.



Fifty-Gallon Aluminum Autoclaves Used as Culture Vessels during Part of Growth of the *Clostridium*

The immense present size of the butanol industry, founded as it is on a minute microörganism, and its further growth must be a continuing source of wonder. Already two gigantic plants are turning out a combined total of more than 100 tons of solvents per day, and every effort is being made to increase this by 24-hour days and 7-day weeks. A further increase of plant—already more than doubled during the past twelve months—is being planned, and the end is not yet. Quite as remarkable is the youthful lacquer industry, which has already grown to the proportions of consuming 60 tons of butanol per day and of calling for more, although butanol and lacquers as we now know them were scarcely more than museum specimens a very few years ago. Not only is this industry great of itself and by supporting another, but the fact that its raw material is in a sense a waste makes it a decided economic asset to the country. Corn, most largely used as a feed and a food, as produced is not always fit for these purposes and large quantities must be utilized otherwise. Before 1918, this low-grade corn went largely into the manufacture of whisky and starch with its by-products, but now the butanol industry has become one of its largest consumers.

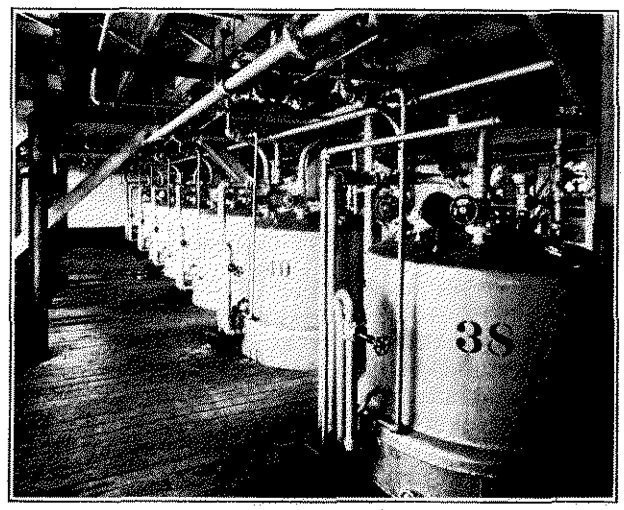
Outstanding Characteristics of Plant

In a plant carrying out the processes about to be described, one is struck by two things: the careful engineering to make every operation economical to the last degree; and the scrupulous neatness and cleanliness of those parts of the plant given over to the fermentation process. Both are inherently essential to the proper carrying out of the operation, but nevertheless one seldom sees in any plant so economical a use of power and the almost surgical cleanliness practiced here. The power for operation is generated in seven 500-horsepower Sterling boilers, and since the majority of it is required as steam at comparatively low pressure for process use, two 1500-kilowatt turbo-generators are used for the dual purpose of supplying the needed electrical power and of reducing steam from boiler to process pressure. By this shift electric energy is delivered to the plant at a cost surprisingly low as compared with accustomed values. Water is pumped at a rate of 60,000 gallons per minute from twenty-one deep wells and, in addition, mechanical power is supplied by the turbo-generators through individual motor drive for grinding and sifting the corn and for the operation of conveyors and stirrers as well as for lighting. The single point in the process where pumping is necessary is in the feed to the continuous "beer stills" and this is accomplished by reciprocating steam pumps.

Raw Materials

Low-grade corn, unfit for feeding purposes, forms the basic raw material used in this process. Other carbohydrates may be used with corn if market conditions justify it. The corn is screened to remove fine matter, passed over a magnetic separator to remove tramp iron, and finally ground through roller mills. The output of the mills is screened to separate the fine portion, and the coarse particles are returned for further grinding as necessary. The bran separated from the fine starch particles is passed through dryers and sold for feed. The fine meal is conveyed to overhead bins from which it is weighed into the process.

In addition to the use of whole corn, a part of the corn may be degermed and only the starch returned to the process. Only a small part of the corn used may be thus treated as too great a reduction in the amount of protein in the mash would be objectionable, protein being essential in the diet of the microörganisms. The degerming process yields value which more than pays for the cost of recovering it.



Thousand-Gallon Welded Steel Tanks Which Are Inoculated from the Fifty-Gallon Batches

Mashing

Meal from the overhead storage is weighed to a conveyor which carries it directly to the mashing tuns. These are five large, open steel kettles of a capacity a little more than 10,000 gallons each. They are charged with 6100 pounds of meal in 10,000 gallons of warm water (71° C.), heated in exchangers by the hot mash on its way to the fermenters. From the mashing tuns the charge is dropped into cookers, which are closed autoclaves provided with motor-driven rake agitators. In the cookers the charges are cooked for 2 hours by live steam under pressure, and toward the end of this period the pressure is raised for positive sterilization and the charge blown by its own pressure to the fermenters. In passing to the fermenters, the sterile starch solution is cooled in a heat exchanger of the concentric pipe type, and its temperature reduced to about 98° F. (37° C.), the heat given up by the mash being absorbed by fresh water on its way to the mash tuns. The starch solution at this point is about the consistency of ordinary flour paste. It is essential to note that no malt is used and that the solution contains starch and not sugar.

Fifty Gigantic Fermenters (50,000 Gallons Each) Perform the Final Plant Conversion of Corn to Solvents

As the subsequent process depends upon the growth of a microörganism it is especially necessary that the mash be completely sterile until inoculated with the desired culture. The cooking process not only dissolves starch but also sterilizes the solution, and from the cookers to the end of the process every possible precaution is taken to prevent contamination by wild yeasts. Every pipe line, storage vessel, and fermenter is completely sterilized by live steam each time a charge has passed through. In the construction of pipe lines to carry the mash no pumps are used and particular care has had to be exercised to prevent the formation of pockets in which the mash might collect and form a medium for the accumulation of any undesired bacteria.

Growth of Culture

The *clostridium acetobutylicum* (*Weizmann*) which accomplishes the fermentation of starch solution to normal butanol, acetone, and alcohol is very carefully watched during its growth from a spore for 5 days on five successively larger quantities of medium before it is put into the final fermenters. This is necessary to be sure that each fermenter is inoculated with a pure, vigorous strain which will perform a proper fermentation and which is not contaminated with any other microörganisms. It has been found best to supply the fermenters used in plant practice with cultures not more than 6 days old grown from spores. This, along with the danger of contamination of the culture, necessitates very careful bacteriological control and care for the growing culture.

The process of growth of the *clostridium* begins with the inoculation of soil from a pure culture for the formation of spores. The soil is inoculated and then carefully dried to promote spore formation. A small particle of this soil is used to inoculate a starch solution in a test tube. This is shocked at boiling temperature for an instant, and cultured at 37.5° C. for a day. It is then transferred to 500 cc. of medium and again incubated for 24 hours. The culture in 500 cc. is grown at body temperature in 6 liters of mash for still another day. If the culture has followed a normal course to this point, 50 gallons of mash are inoculated with it, and even more careful control of acidity and gas formation is exercised. After a day in the 50-gallon container, the culture is transferred to a 1000-gallon container where it spends another day developing before it goes into the final 50,000-gallon plant batch. The fermentation of the plant batch requires about 2.5 days and is allowed to proceed until gas evolution ceases.

The utmost care is exercised throughout the bacterial process to be sure that the *clostridium* strain is vigorous and pure. The first three cultivations from the spore are carried out in glass and the mash used is especially prepared in the laboratory. These are carefully watched throughout their incubation periods but no definitely chemical control is exercised over them. Naturally a sufficient number of cultures is made originally so that a few may be discarded before they spoil large batches of mash if they should turn out to be abnormal in any respect.

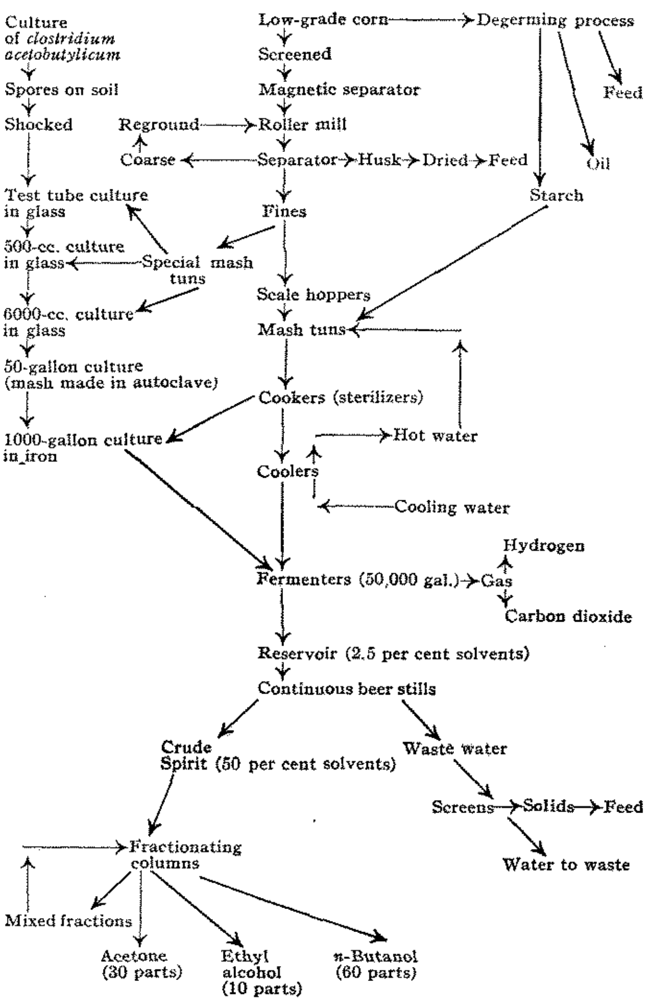
By the time the *clostridium* is ready to be put on 50 gallons of medium, one is definitely sure that no organisms other than *clostridia* are present. The inoculation of 50 gallons is carried out in forty-eight 50-gallon aluminum autoclaves provided with jackets for steam or water. They are so arranged that the mash is cooked in individual batches, and the cooking process, followed by cooling to incubation temperature, is carried out in the same vessel. The growth of the *clostridium* on this medium is controlled for acidity and gas evolution. Both should follow definite curves, and it is easily possible to be sure that the culture is properly active by a comparison of its curves of acidity and gas evolution with predetermined normals. If this growth is as it should be, the charges from the 50-gallon autoclave are run into forty-eight 1000-gallon steel fermenters containing the same medium used in the plant operation. Here, too, acidity and gas evolution are watched closely to determine the microbe's activity on the large-sized batches.

The *clostridium* having gone through these preliminary cultivations, should have definitely shown that it is equal to the task of converting a large batch of starch into solvents. If it has not, the culture is discarded. The large fermenters are forty-eight 50,000-gallon steel tanks with rounded ends, reminding one of the usual overhead municipal water-supply tanks. Before being charged with sterile starch solution, these tanks, as well as those used for the preceding cultures, are carefully sterilized with live steam and later blown out with sterile compressed air to insure their complete cleanliness and sterility. After charging, the fermenters are closed with a water seal to prevent access of air, which might bring in contaminating bacteria, and to permit venting of the carbon dioxide and hydrogen formed. During the fermentation in the large batches, acidity and gas evolutions are carefully controlled so that any batch which does not follow a regular course can be separated from the rest and proper disposition made of it.

The *clostridium* converts 3 pounds of starch into 1 pound of mixed solvents in the form of a 2.5 per cent solution. During this conversion, a mixture of 45 per cent hydrogen with 55 per cent carbon dioxide is evolved. The solvent mixture, obtained as a 2.5 per cent solution, is made up of about 60 per cent butanol, 30 per cent acetone, and 10 per cent ethanol.

From the fermenters the solution is passed to an underground reservoir of 80,000-gallon capacity, from which it is pumped to the continuous beer stills. At no other point is the mash pumped. These stills are three 96-inch columns 54 feet high, and turn out mixed solvents containing about their own weight of water. The feed to these columns is through two reciprocating steam pumps, whose operation is controlled by the operator at the tops of the stills. The action of the pump makes and breaks an electric contact which flashes a light on the control board and this enables the operator to follow them at a distance. The waste from the beer stills contains a small amount (about 1 per cent) of the non-starchy parts of the corn grain, and this is passed over a fine sieve to remove large particles for feeding purposes, the balance being run off to the sewer.

Flow Sheet for Butanol Production



The 50 per cent solvent mixture is passed from the continuous stills to temporary storage to be later fractionated in discontinuous column stills. The fractionation of the mixed solvents is made easier by the fact that butanol and water form two layers when mixed and part of the concentration of solvent is accomplished by taking advantage of this, the two layers being distilled separately. Otherwise the fractionation follows a regular course.

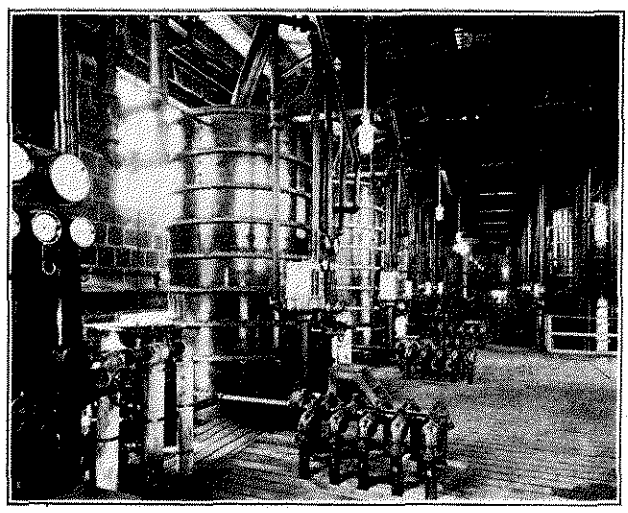
By-Products

By-products appear at three points in this process. The first is the husk separated from the corn in the grinding process; the second is the mixture of hydrogen and carbon dioxide generated in the fermentation; and the third is the slop from the "beer" stills. In addition to these three, the germ of the corn, which may be separated before its starch is used, might be listed, but it is not, strictly speaking, a by-product of the operation since only a relatively small part of the protein may be removed from the corn before it goes into the process. The disposition of the husks as feed after drying has already been mentioned. The recovery of value from the gas mixture and from the still slop are more complex problems.

The large quantities of mixed hydrogen and carbon dioxide generated during the fermentation and the surprising purity of this mixture have led to intensive research for their utilization. Naturally, the hydrogen has the greater value and the recent rapid development of processes for the synthesis of ammonia suggested themselves as profitable means for its utilization. The separation of the carbon dioxide from the hydrogen was readily solved by passing the gas mixture under pressure through a tower down which water trickles. This dissolves practically all of the carbon dioxide, leaving the hydrogen so nearly pure that a treatment with caustic soda solution economically removes the remaining traces. This operation requires considerable power for compression, and since the carbon dioxide itself is practically worthless, the solution of it under pressure is passed through a Pelton wheel to recover some 60 per cent of the energy previously absorbed. In this pure form the hydrogen may be used for ammonia synthesis without difficulty and the nitrogen required may be easily obtained in a satisfactorily pure form by burning a part of this hydrogen in air.

It is also easily possible, by passing the mixed gases over heated carbon, to procure a mixture of carbon monoxide and hydrogen which might serve admirably as a raw material for the synthesis of methanol, if desired. Other possibilities suggest themselves, but these two seem to offer the greatest promise, and a plant utilizing this waste gas mixture for ammonia synthesis is already being built.

The slop from the beer stills contains about one per cent total solids. Part is in suspension and may be readily removed by passing the slop through a fine wire screen. The particles thus collected have a nutrient value and may be



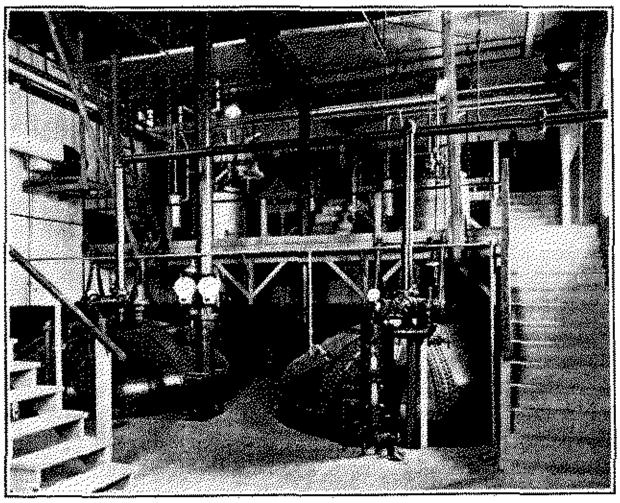
Fractional Distillation to Separate the Three Solvents—a Huge Still Plant

sold for feeding purposes. The part of the solids in so weak a solution offers considerable difficulty in recovery. Investigations are being made to concentrate these portions of the residue by using this filtered slop to replace fresh water in preparing the mash for the fermenters. If this succeeds, the concentration of the solids in the slop can be readily doubled, and hence the cost of evaporation for their recovery can be correspondingly reduced. At present, the dissolved solids in the slop are not recovered because of the high cost of evaporation and the low value of the product.

Research and Control

So large an operation must necessarily be carefully controlled, both chemically and bacteriologically, and for this purpose competent chemists and bacteriologists constantly watch the progress of the process. The bacteriological control laboratory prepares the cultures *in vitro* which are later to go into the plant and supervises them to detect and correct any contamination. The chemical laboratory exercises control over raw materials, over the acidity and gas evolution of cultures once they have gotten into the larger units on the way to the plant, and over the distillation processes and products.

Research, which has been so important in the original development of this industry, is not neglected in its present operations and future plans. Research bacteriologists are constantly studying the *clostridium* and its habits of growth with a view to increased plant yields and in the hope of being able to shift production as demand shifts from one of its products to another. Chemical research goes into a variety of phases of the process and the utilization of the materials produced. The research department operates a complete semi-commercial unit (one-fourth plant size) for trying out promising modifications of the process before they are put on full plant scale.



A Complete Pilot Plant Is Available for Testing New Developments

The utilization of the solvents produced is a subject of extensive and intensive research. Lacquers are made up and tested under a variety of conditions for the assistance of manufacturers, and this is assisting materially in the development of the lacquer industry, both in technic and in supplying new solvents. The research department has developed auxiliary plants for preparing derivatives of butanol and acetone on a small commercial scale and butyl aldehyde, dibutyl phthalate, and diacetone alcohol are now made in them. It is prepared to undertake other syntheses from time to time as need arises.

The pressing problem of the research department, and one whose solution is soon to be put on a commercial scale, is the utilization of the gaseous by-products of the fermentation. A complete train for separating hydrogen and carbon dioxide from the mixture as evolved and apparatus for conducting gas reactions at pressures up to 5000 pounds per square inch form part of the research department's equipment for these studies. Already a plant for ammonia synthesis is being built as a result of these researches, and it is probable that other processes of commercial importance may be developed. Certainly, so active a research organization assures the profitable permanence of this new industry.

Acknowledgment

The details of this story were supplied by Chas. L. Gabriel, T. P. Walker, and H. E. Perry, of the Commercial Solvents Corporation. The author is greatly indebted to these gentlemen for information given, for permission to visit that corporation's plants and research laboratories at Terra Haute, Ind., and at Peoria, Ill., and for many personal courtesies.

A Constant-Level Water Bath Using Distilled Water[1]

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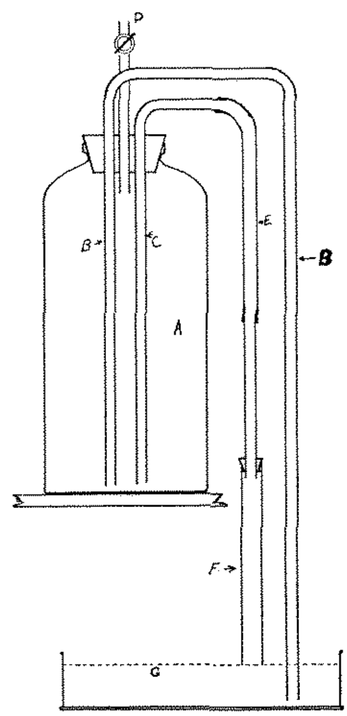
Tap water carries so many impurities that readily precipitate out on evaporation that it has proved objectionable when used in a water bath. To overcome this objection an apparatus was developed whereby distilled water, kept in a bottle at a considerable distance from the bath, was used as a source of supply.

The apparatus consists of a large 10- or 15-liter bottle, *A*, supplied with a 3-hole stopper. A short tube, *D*, with a stopcock or pinchcock is fitted to the stopper and used to fill the bottle and start the siphon. Glass tube *B* runs from the bottom of the bottle to the bottom of the water bath, *G*. Tube *C* runs from the bottom of the bottle through the stopper to rubber tubing, *E*, which is fitted by glass tubing and stopper to a large-bore glass tube, *F*. This tube must be at least one inch in diameter to overcome any capillary attraction. Tube *F* is adjusted so the bottom of the tube is just at the level at which it is desired to keep the water in the bath, here represented by the dotted line.



To start the apparatus, bottle *A* is filled, a pinchcock is clamped to rubber tube *E* to close *C* and *F* temporarily, the stopcock on *D* is opened, and pressure applied till the water begins to siphon through *B*. The stopcock at *D* is then closed and the pinchcock on *E* removed. The water will then flow through *B* into the water bath until it reaches the lower level of tube *F*, rising in tube *F* to a level with the bottom of *C* in the bottle. Atmospheric pressure will be balanced and the water will stop flowing until it again drops below *F*.

Obviously, tubes *E* and *B* may be lengthened considerably, thus providing for placing bottle *A* a considerable distance from the bath.

Water bath *G* may be heated by electricity or gas.

[1] Received July 19, 1926.