

Boat and Machine Company. We have several tank cars in shuttle service to transfer the caustic to the plant.

Because of the nature of the material being handled, several precautionary measures are taken to insure safe operations, *e.g.*, the caustic is sampled in the barge before unloading. Since there is usually a fairly strong breeze on the river, the sample man must be sure he is on the up wind side of the manhole to prevent the caustic from being blown from the sampler rod onto him. Proper clothing and protective devices are also a prerequisite to safe handling. Cotton clothing, rubber gloves, rubber shoes, and goggles are worn by the sampler and the pumper. All instruments and handling equipment are washed immediately after use.

The cars are weighed into the plant and spotted on a railroad siding adjacent to the caustic storage tanks. Here special (Paranite wire-reinforced, alkali-resistant) hose with safety clamps are connected to the discharge line on the bottom of the car. The cars are also fitted with safety locks in addition to the regular foot valves on the outlets. The caustic is unloaded by centrifugal pump into storage. Two of our storage tanks have a capacity of 1,530,000 lb. each. There are also two smaller tanks with a combined capacity of 1,255,000 lb. Our storage tanks and lines are of black iron construction, and all caustic lines are painted a color that identifies them from the maze of lines in our Raw Stock Department. All pumps have guards, and every flange has a metal seal around it to prevent spraying if a gasket should go.

From our storage center, caustic is disbursed to the points of usage throughout the plant. The majority of the caustic is used at full strength (50° Bé); however there are some operations which require weaker solutions (refining), and special diluting facilities are provided for these.

*Salt (NaCl)*. A concentrated brine solution (pickle to the soap industry) is used in the graining of soap in the boiling operations. The salt is received in hopper cars in the form of rock salt. The car is spotted over a pit, from which the salt is conveyed by a screw conveyor into the salt lixiviator where water is added to dissolve the salt. The pickle is then pumped to wooden storage tanks, preparatory to using it in the kettles.

### Conclusion

No laboratories are deeper in research than those of the soap and synthetic detergent manufacturers. W. L. Sims, president of Colgate-Palmolive Company, was quoted recently in the New York press as follows: "probably 70% of the volume in our business today comes from products that didn't exist 10 years ago. The same thing will be true 10 years from now."

This statement bears out the ever-changing dynamics of the industry. Much of the equipment and many of the materials covered in this presentation did not exist a few years ago, and as research and engineering create new and improved products and new and improved automated equipment, our means of handling these and other raw materials, even though they represent the best available today, will be replaced by even more efficient methods and equipment.

## Recovery and Purification of Glycerol

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IN A DESCRIPTION of the recovery and refining of any product it is well to define the end-product. U.S.P. Glycerine of highest purity may still contain 1-2% water but must retain only small amounts of other organic or inorganic impurities. Any such traces which might make it unfit or unattractive for human consumption are rigidly defined. Specifications for grades of refined glycerine most generally accepted in this country are United States Pharmacopoeia (U.S.P.), Chemically Pure (C.P.), High Gravity Dynamite, and Yellow Distilled.

Probably the most widely quoted in this country is the specification for U.S.P. glycerine, which is substantially C.P. glycerine. Among other requirements the product shall contain not less than 95% of glycerol<sup>1</sup> and shall have a



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specific gravity not less than 1.249 measured at 25°C. Tests are defined and limitations set on non-volatile residue, ash, carbonizable substances, neutrality, chlorides, arsenic, heavy metals, acrolein, glucose and ammonium compounds, fatty acids and esters, color and odor.

The United States Federal Standard Stock Catalogue O-G-491 gives detailed requirements of high gravity glycerine (dynamite glycerine). The specific gravity shall be not less than 1.2620 at 15.5/15.5°C. This corresponds to 98.7% glycerol. The color shall be not greater than 80 Y 20 R on a 5½-in. Lovibond scale. Also delimited are appearance, odor, acidity or alkalinity, ash, and chlorides.

The same catalogue gives the following detailed requirements for yellow-distilled glycerine. The specific gravity shall be not less than 1.2550 at 15.5/15.5°C. This corresponds to 96% glycerol. The color in a 5¼ in. depth shall be not greater than 80 Y 20 R on the Lovibond scale. Also delimited are ap-

<sup>1</sup> The term glycerol is accepted as a proper commercial name for the compound  $C_3H_5(OH)_3$  and designates it as a chemical substance or as a descriptive adjective. The term glycerine applies to commercial products of glycerol of whatever grade or degree of purity. Soap lye or spent lye describes the alkaline-brownish liquor containing small quantities of glycerol settled from the soap-boiling process. Sweetwater is the term for glycerol containing waters from Twitchell or Autoclave splitting of fats.

pearance, odor, acidity or alkalinity, ash, and chlorides.

While processing methods are set up primarily to cover these grades, modifications of the requirements are frequently made to fulfill specific needs. In some cases, particularly where food products, pharmaceutical and cosmetic preparations are concerned, more stress is laid upon odor and color and the manufacturers make extra-quality grades to meet this demand. Glycerol is obtained in the form of a more or less dilute solution accompanied by extraneous substances, some of which have their origin in the oils and fats used as raw materials, others of which are introduced during processing. The first purification step is to remove non-glycerol substances as far as practical by precipitation and filtration; the second step is to concentrate the solution by exaporation; and the third is to effect purification to the desired degree by distillation and bleaching.

In commercial operations the glycerol liquors produced by the various methods may range from 2 to 20% glycerol. It is evident that the more dilute the solution, the greater the expense of evaporating the excess water. The procedure employed is set up to recover as high a percentage of glycerol as profitable in the most concentrated form practical. The kettle system of soap boiling has been modified over the years with this objective, progressing from the direct flow to the countercurrent system and for still more efficiency to the continuous centrifugal system. In these instances the concentration of glycerol in the lye has been increased successively from 2 to 3%, common practice a number of years ago, to 4 to 6% when the direct flow system is used, then to 8 to 13% with the countercurrent system, and lately to 12 to 15% when the continuous centrifugal system is employed. Progress in hydrolyzing fats has likewise resulted in increasing the glycerol in the sweetwaters. For years 8 to 12% concentration of glycerol obtained by the Twitchell process was considered good, but it is now practical by high-pressure continuous autoclaving to obtain a concentration of 12 to 20%. As a consequence, a considerable amount of steam is saved in evaporation and some economies are effected in costs of treating the lyes or sweetwaters.

Substances, besides those added in processing, which must be removed during the purification and refining of glycerol are the impurities and residues of fatty matter accruing from the original fats. The impurities ordinarily consist of fatty acids dissolved in the glycerol liquors, resinous and nitrogenous compounds, color bodies, hydrocarbons, and fermentation products of fats and glycerol, such as trimethylene glycol, lactic acid, succinic acid, oxidized fatty acids, fatty acids of lower molecular weight than the original acid, aldehydes, and ketones.

In soap boiling the lyes carry away a substantial amount of impurities and coloring matter from the soap during the various changes. In the hydrolysis of fats relatively fewer of the impurities associated with the fats are carried into the glycerol sweetwaters than is the case with soap lyes, but in both instances some coloring matter and other impurities are present prior to treatment for their removal. Substantially all of the impurities present must be removed to produce the better grade of glycerine.

Another important point to be observed is the prompt treatment of dilute glycerol liquors, particu-

larly those from very poor stock. Serious fermentation losses of glycerol may occur if they are kept in storage for too long a period or are stored under unsanitary conditions.

Regardless of the grade of raw stock or the method used in processing it, the final quality of finished glycerine is greatly affected by the chemical control and manipulation of the various steps in recovery and purification. Of first importance is the maximum removal of organic impurities from the dilute glycerol liquor by chemical treatment and filtration prior to concentration. Sanger (1) points out that a wholly untreated spent lye on concentration will produce a crude glycerine containing about 40% glycerol and an excessive amount of organic impurities. Such a product can yield only an inferior quality of glycerine on distillation, and the excessive loss of glycerol in foots would make manufacturing costs prohibitive. To a lesser degree, inadequate chemical treatment, found in some of the smaller soap plants, will yield an inferior crude glycerine, which at times is not acceptable or is sold at a discount to the glycerine refiners. On the other hand, it is possible by skillful chemical treatment to upgrade the quality of glycerine derived from low-grade stock.

The chemicals most commonly used to remove impurities from glycerol liquors are alum, ferric chloride, calcium chloride, lime, soda ash, sulfuric acid, muriatic acid, and caustic soda. The aluminium and iron salts serve as coagulants and precipitants. The other chemicals also serve as precipitants and neutralize and regulate the acidity or alkalinity of the treatments. Diatomaceous earth is sometimes used for a mechanical aid in filtration. The choice of particular chemicals for treatment depends on their application and cost.

### Spent Lye Treatment

The treatment of spent lyes has been described by several writers during recent years, but in view of its importance with relation to the quality of the finished product a review of modern methods is worthwhile. The treatment consists of a series of operations designed to remove nearly all of the organic impurities from the lye. As a first operation the spent lye is commonly boiled with fatty acids or high fatty acid stock to reduce the content of free caustic and soda ash. Next the lye is allowed to cool, and solid soap is skimmed off. Following this, the lye is usually given the "double treatment" although, in cases where very poor stocks are being worked, the lyes may be given a preliminary chemical treatment with calcium chloride and lime to remove a portion of the impurities. The double treatment consists of two steps: a) the addition of an acid and a coagulant, followed by filtration which removes the bulk of impurities, and b) the addition of caustic soda to the filtrate to precipitate and remove the balance of coagulant in solution and to regulate the pH of the liquor to a point where it is least corrosive in subsequent process equipment.

It is common practice, particularly in the larger soap plants, to boil the spent lye in a kettle with high fatty acid stock to reduce any residual free caustic and neutralize the sodium carbonate in the lye. The fatty acids react readily in the boiling lye. Soap from several operations may be accumulated as part of the stock for a regular kettle. If fatty acids or high fatty acid stock are on hand for soap-making, the two-fold

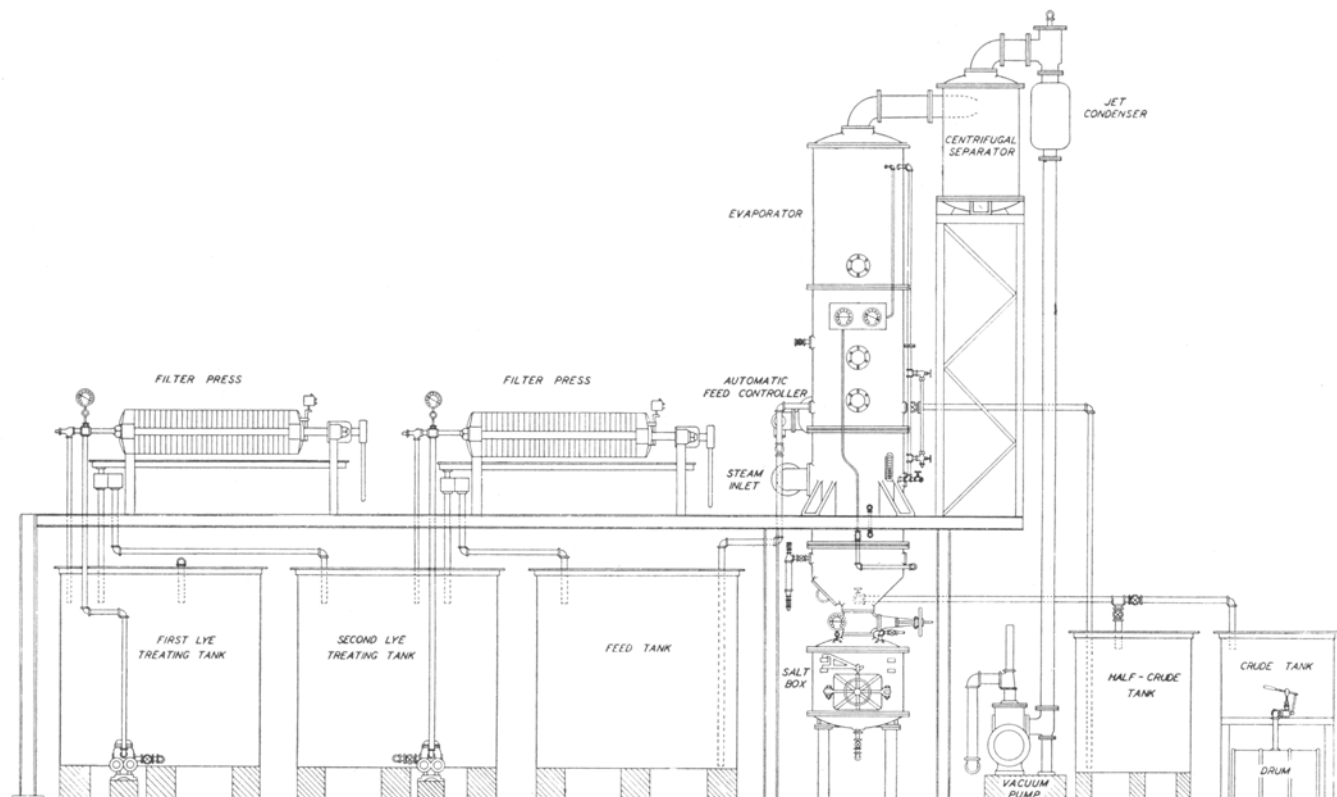


Fig. 1. Spent soap lye plant by Wurster and Sanger.

economy of this operation is apparent. The caustic in the lye which would ordinarily be wasted is salvaged, and the amount of acid required for neutralizing it in subsequent treatment is reduced correspondingly.

The spent lye, which may or may not have been subjected to a preliminary fatty acid treatment, is discharged from the kettle house to storage, where the hard soap which separates and rises to the top of the storage tank is skimmed off. The skimmed soap is returned to the soap kettles.

It is assumed that the spent lye treated in a typical plant is of good quality, derived from boiling tallow and coconut oil soap and from a three- or four-wash countercurrent system in the kettles. The spent lye will contain 7-9% glycerol and, with no preliminary treatment of the lye with high fatty acid stock, will generally run between 0.15 and 0.25% total  $\text{Na}_2\text{O}$ .

In the plant illustrated (Figure 1) a charge of 100,000 lb. of lye is pumped to the acid treatment tank.

The first treatment is carried out as follows.

A suitable amount of either sulphuric or hydrochloric acid is added with vigorous air agitation until the lye is at a pH of 8.0. At this point sufficient alum or aluminum chloride is added for good coagulation of the impurities. The alum can be added directly or, better, dissolved in water and drained into the treatment tank. After the chemicals are added and thoroughly mixed into the treatment, a sample is withdrawn and filtered. The filtrate should be clear, nearly colorless, and have a pH of about 4.5 to 5.0 although a somewhat wider range is often found in practice. The addition of a slight excess of hydrochloric acid should produce no precipitate. If insufficient alum has been used, the filtrate will be cloudy. Enough should be used so that the filtrate will be clear and an excess remain to form a floc in the second treatment when caustic soda is added. When the batch has been satisfactorily adjusted, the treated liquor is then pumped through the acid-treatment filter press. Ferric chloride is sometimes substituted for alum in the first treatment of spent lye.

In the second treatment caustic soda is added to the acid-treated filtrate until alkaline to phenolphthalein (pH 8.5 to 9). This will cause the small quantity of dissolved alumina to separate as a flocculent precipitate.

Excess alkalinity will cause glycerol polymerization during evaporation of the lye and later in the distillation of the crude. Excess acidity will allow some of the fatty acids remaining from the treatment to distil with the glycerol. After the caustic soda has been added and well mixed into the treatment, a sample is withdrawn and tested to see if it is just alkaline-to-phenolphthalein indicator. The treated liquor is then pumped through the alkaline-treatment filter press. The filtrate is circulated to the original tank until clear.

There is a disadvantage in the use of alum and sulphuric acid in that they react with the alkali of the lye to form sodium sulfate, which becomes an objectionable impurity in the salt recovered during the evaporation of the purified lye. The salt is generally reused in graining out kettle soap and contains an appreciable percentage of adhering glycerol liquor, some of which may be lost in kettle operations. The presence of sodium sulfate in the recovered salt increases the percentage of glycerol retained and may result in a correspondingly greater loss of glycerol from this source. Further, as the percentage of sodium sulfate builds up to 12 or 15% or more, it interferes with the proper operation of salt separators and also reduces the effectiveness of the salt in graining out soap in the kettles. When the salt is no longer satisfactory for use, it is discarded.

A simplification of the double treatment of spent lyes described is the single treatment, which has been used to a considerable extent. The coagulant and acid are added in the same manner as in the double treatment, but, as usually practiced, the quantity of acid used is slightly less than required to neutralize the alkalinity of the lye. After a single filtration the

lye is ready for evaporation; the filtrate is slightly on the alkaline side. While the single treatment requires less equipment and labor, the results are not as dependable as those obtained by double treatment.

A variation of the single treatment utilizes a slight excess of acid so that the filtrate is on the acid side. While there are certain advantages in evaporating an acid liquor, the corrosion problems have been serious. In recent years however the development of corrosion-resistant metals has overcome this difficulty. The object of evaporating on the acid side is to remove by volatilization a substantial proportion of the fatty acids which persist through normal treatment and remain in the treated lyes, thereby reducing the quantity of these impurities which go to the still. The fatty acids are difficult to separate completely from glycerol during distillation, and appreciable amounts of fatty acid esters are often present in distilled glycerol, probably as the monoglycerides, which have boiling points close to that of glycerol. The lower acids, such as butyric, valeric, and caproic, impart unpleasant odors to glycerol, particularly when their esters are hydrolyzed to the free fatty acids.

### Sweetwater Treatment

In general, the sweetwaters from autoclaving are readily purified and require less treatment than those from the Twitchell process, where considerable mineral acid is present. The use of the catalysts, zinc oxide, lime, magnesia, and the like, do not affect the treatment of the sweetwaters because the insoluble metallic soaps become a part of the fatty phase.

Ordinarily the sweetwaters from autoclaving are settled and skimmed of dirt and insoluble fatty material. This is preferably followed by a light treatment with lime to precipitate dissolved fatty acids and neutralize the liquor to the phenolphthalein endpoint (pH about 8.5). The alkaline liquor is then filtered and evaporated to a 90% crude glycerine. However if caustic soda is used, the sweetwater will contain soluble sodium soaps that must be removed by precipitation with lime followed by filtration. Or the sweetwater may be treated in the same manner as spent soap lye, that is, with alum followed by neutralization with caustic.

It is current practice in several large installations, where continuous autoclaves are used, to evaporate the sweetwater directly from the autoclave without previous treatment.

### Concentration of Glycerol Liquors Single and Double Effect Evaporation

The dilute glycerol liquors, after being purified, are concentrated to crude glycerine by evaporation. This is usually carried out in conventional, natural circulation evaporators under reduced pressure and with low-pressure steam as the heating medium. Glycerol liquors may be divided into two general classes: a) spent lye which deposits salt crystals on concentration and therefore requires a salting-out type of evaporator, and b) sweetwaters which deposit at the most only a small amount of sludge and for that reason do not require the salting-out feature of design.

The standard vertical, short-tube evaporator, (Figure 2) is especially adapted for salting-out liquors and is the one most commonly used for spent lye. The body of the evaporator is a vertical cylindrical shell, fitted with a cone bottom. The calandria in the

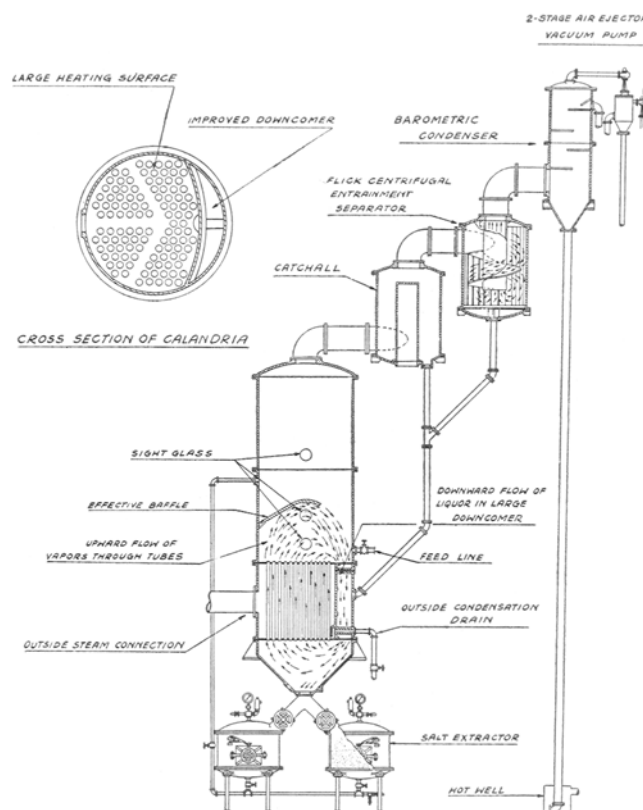


Fig. 2. Wurster and Sanger single effect glycerine evaporator.

lower part of the evaporator consists of a steam chest with tubes  $1\frac{1}{2}$  to 4 in. in diameter and about 4 ft. high. Longer tubes tend to salt-up more readily. Steam condenses on the outside of the tubes, giving up its heat and causing a natural circulation of the liquor upward through the tubes and then back through the downtake. The downtake is a vertical passage through the calandria and may be centrally or eccentrically located or, in the case of a basket type of calandria, consists of an annular space between the evaporator shell and calandria.

At the bottom of the evaporator means is provided for disposing of salt, which forms as the spent lye is concentrated. Generally this is done by allowing the salt to settle as a slurry from the cone into a salt box equipped with a discharge valve and separated from the bottom of the evaporator by another valve. The slurry which collects in the salt box is blown periodically, as required, with air and steam to salt-handling equipment for separating the glycerol liquor from the salt. In an older type of salt box the salt is filtered on an internal screen, washed, steam-dried, and finally scraped out manually through a door in the side of the salt box.

In the larger plants it is customary to concentrate glycerol liquor in double-effect evaporators (Figure 3) because of the savings in steam and condensing water. Generally it can be shown that the savings justify the additional installation of the second effect.

Besides economy, a double-effect evaporator has an added advantage in flexibility. The vapor piping and auxiliary equipment may be so arranged that the double effect can be operated as two single-effect evaporators. Then, in times of peak production, double the quantity of glycerol liquor can be handled. There

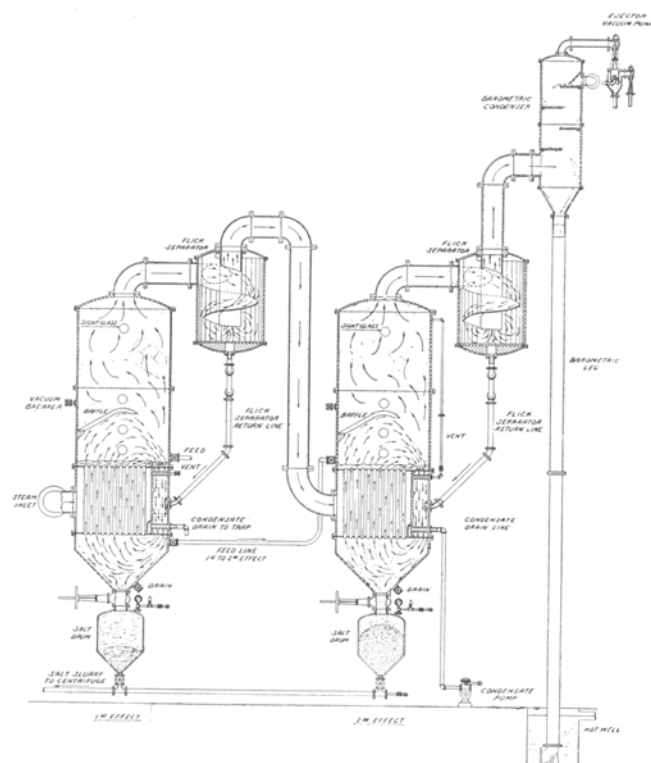


Fig. 3. Wurster and Sanger double effect glycerine evaporator.

is no savings in steam over that required in a single effect.

In normal operation, glycerol liquors are concentrated in two steps. First, they are brought to a "half-crude" state and discharged from the evaporator to a holding tank. The half-crude contains 30-40% glycerol and is accumulated until sufficient to return to the evaporator and finish to crude. It is not desirable to attempt to go from weak glycerol liquor to crude in one step since the evaporation rate is greatly retarded in the later stages as the liquor becomes more concentrated. A better over-all rate of production is possible with two-step concentration. In double-effect operation the two evaporators may be operated as individual single effects for concentrating the half-crude to finished crude. However, for more economic utilization of equipment, it is preferable to provide a smaller, single-finishing evaporator and operate the double effect continuously.

Two-step concentration of the glycerol liquors also facilitates the subsequent processing of the salt that is crystallized. The major portion of the salt is dropped out in going to the half-crude state while at the same time the crystals are larger and more easily washed and drained by virtue of having been crystallized from a solution containing less organic matter.

In the typical spent soap lye evaporator plant each evaporator is equipped with a salt box in which the salt, as it crystallizes and settles, accumulates as a slurry in glycerol liquor. When a salt box is nearly filled with salt slurry, as indicated by sight glasses on the side of the salt box, the valve between the evaporator body and the salt box is closed and the contents are blown by air pressure to a salt slurry tank. This transfer can thus be made without interfering with the operation of the evaporator. In the tank the slurry is kept well agitated or under constant circulation by means of a pump to prevent the salt

from settling into a compact mass which cannot be pumped. A portion of the circulating slurry is diverted to the centrifugal salt separator. The effluent from the centrifuge, consisting of glycerol liquor and wash water, is collected as half-crude and is sent to the evaporator for finishing to crude glycerine. The dry salt is available for reuse in the soap kettles. The centrifuges employed in making this separation are of three basic types: the continuous, the fully automatic batch, and the older basket-type of batch machine. Other methods of separation are still used, particularly in smaller plants.

Of the continuous centrifuges made by the Bird Machinery Company and commercially used, the screen type and the solid bowl type are most common. The former consists essentially of a cylindrical, filtered drum or screen, within which is mounted the conveying drum or plow. Both members rotate on a horizontal axis in the same direction; the conveyor moves at a somewhat slower speed than the filter. The salt-glycerol slurry enters at one end, between the two drums, and is spun against the screen. Filtrate passes through, and the salt is retained. The plows mounted on the conveyor drum move the cake slowly along the filter screen to the discharge end. Spray nozzles mounted on the conveyor drum apply wash water.

The more recent design is the continuous, solid-bowl type (Figure 4). The basic operation of this

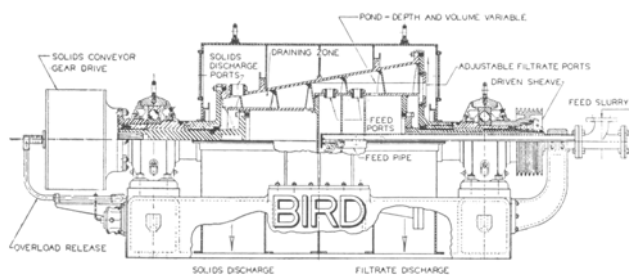


Fig. 4. Cross section of the Bird continuous centrifugal filter.

type is essentially the same as the screen type. The bowl is the container or trough in which the sedimentation takes place. The screw conveyor rotates inside the revolving bowl at a somewhat slower speed than the bowl itself. At the small end of the cone-shaped bowl there is a series of openings or spouts through which the separated solids are discharged. On the base of this truncated cone is another series of openings, through which the clarified liquor flows. The conveyor screw rotating relatively slower inside of the bowl packs the solids and moves them toward the small end. Wash liquor may be applied to the solids to the points where they leave the pool and the discharge ports.

#### Refining or Distillation of Glycerol

The vapor pressure of anhydrous glycerol is 760 mm. at 554°F. Since glycerol both polymerizes and decomposes to some extent at 400°F., and increasingly so at higher temperatures, it is not practical to distill it under atmospheric pressure. In order to vaporize the glycerol at temperatures under 400°F. it is necessary to maintain a greatly reduced pressure in the still or to distill with steam. A combination of vacuum and steam is ordinarily used as a matter of economy and for other reasons.

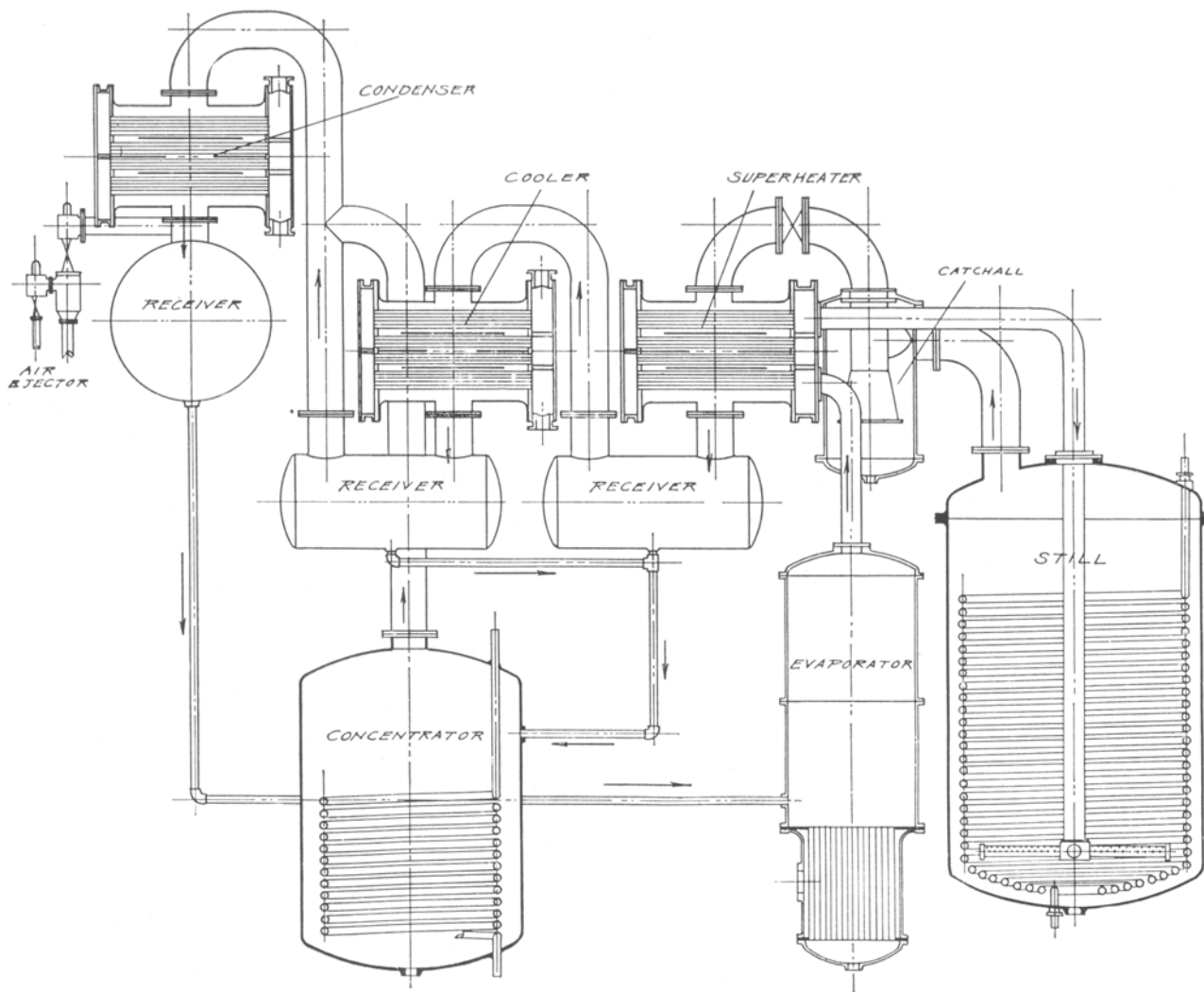


FIG. 5. Garrigue glycerol still.

To distil glycerol it must be heated to a temperature where its vapor pressure is greater than the partial pressure of the glycerol vapors in the still. In the absence of water vapors the partial pressure of the glycerol vapors is for practical purposes equal to the total pressure on the system.

By distilling with steam, the effect is to reduce the partial pressure of the glycerol vapors in the still, assuming the same total pressure is maintained on the still.

In actual practice much more steam is required than indicated because conditions are such that the steam does not become fully saturated with glycerol. Then, also, crude glycerol containing several per cent of salt and organic matter is more difficult to distil because of its viscosity and higher boiling point. The injection of steam is usually desirable to a certain extent in order to agitate the contents of the still.

After the vapors leave the still, they must be condensed, and since they contain considerable water and volatile impurities, in addition to glycerol, it is necessary to fractionate the vapors to recover pure glycerol. It is comparatively easy to separate the glycerol from the water and other more volatile constituents of the vapor by reason of the wide spread in their relative vapor pressures. This is usually accomplished by passing the vapors from the still through a series of condensers, each of which operates at a controlled tem-

perature. The one nearest the still is hottest and the others are progressively cooler. As the vapors pass through each condenser, a partial condensation takes place; the condensate in each instance is richer in glycerol than the vapors passing on to the next condenser. Since the vapor pressure of glycerol is much higher than that of water, relatively pure glycerol is condensed at the higher temperatures, most of the water vapor passing on with a small amount of glycerol to the cold condensers where a dilute solution of glycerol in water is condensed. The purification to a great degree, particularly from those small amounts of volatile substances having boiling points close to that of glycerol, may be carried out by the redistillation of certain fractions or by the use of fractionating columns.

Two systems widely used since the turn of the century are the Van-Ruyambeke system, also known as the Jobbins, and the Garrigue system. A distinguishing feature of the Van-Ruyambeke system is the use of a number of air-cooled condensers for fractionating the distillate prior to its reaching the water-cooled condensers. In the Garrigue system (Figure 5) a distinguishing feature is the recycling of the water vapors from the evaporation of the sweet-water back through the still and the recovery of latent heat from the glycerol vapors. This constitutes an essentially closed system and results in diminished loss and reduced

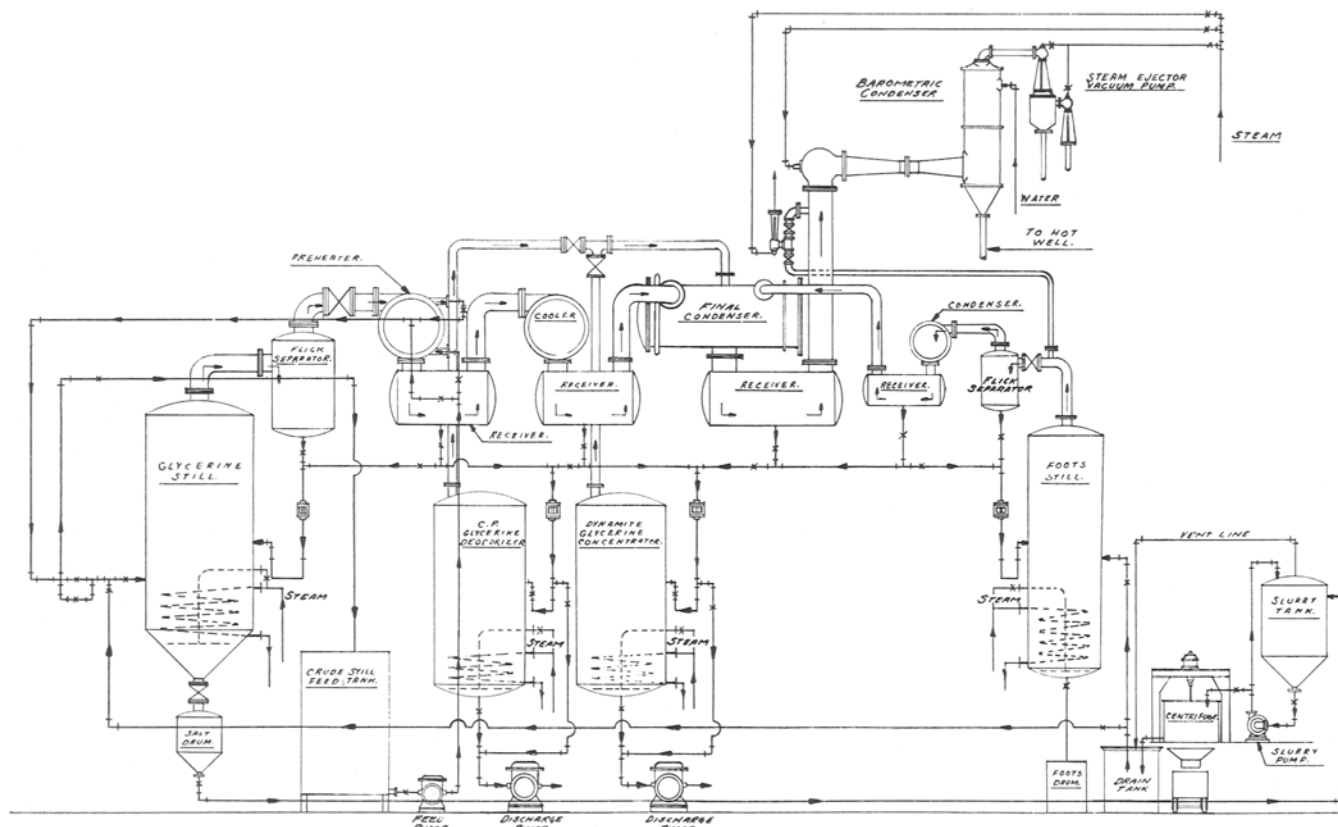


Fig. 6. Wurster and Sanger continuous distillation plant.

consumption of steam. This system also introduced the use of controlled-temperature condensers, which have generally been accepted in more recent designs.

The Ittner still of more recent development contributes to the reduction of steam consumption by use of lower pressures during distillation. This also reduces the percentage of sweetwater produced. A description of this still is found in a paper by Peterson (2) and patents by Ittner (3).

In a closed system it is the practice to continue feeding crude to the batch stills until the salts and other non-volatiles have accumulated to as large a charge as can be finished to foots. The feed of crude is then cut off, and the contents of the still are boiled down, the foots are removed, the still is washed out and the cycle begun again. In a cycle of about 24 hrs. the interruption of normal distillation occupies about one-third of the time. Therefore an increase of the average production of a still is affected if arrangements are made continuously to remove the salt from the contents of the still rather than boil off the glycerol from the salt residue.

Wurster (4) describes a plant (Figure 6) designed to operate in this manner. The general arrangement is similar to the Garrigue except it does not operate as a closed system. As distillation proceeds and the salt passes into the drum below, it is periodically blown as a slurry to a receiving tank and then centrifuged. The glycerol liquor from the centrifuge is boiled down to foots in a separate still. By removing the salt, the total amount of foots is substantially reduced and the percentage of glycerol recovery is somewhat increased.

Fractionating columns have sometimes been used for separating glycerol from water and from some of the impurities. Where it is necessary to improve the

color, odor, and flavor properties of glycerol for food or industrial purposes a second or double distillation is utilized. A column which has met with some success in practical operation is described by Sieck (5).

#### Bleaching of Glycerine

In the crude glycerine is concentrated much of the coloring matter remaining in the glycerol liquors after treatment. The crude consequently varies in color from a straw yellow to almost black, depending upon the source. The preponderant part of these color substances is of a non-volatile nature and is almost completely removed during the course of distillation and fractionation of the glycerol vapors. Some small amount may be carried over as entrainment in the vapors. There is also present in the crude a much smaller amount of color-forming substances which distil with the glycerol. While most of these color substances are separated from the glycerol fractions by partial condensation, a significant quantity condenses with the glycerol, even under the best practical conditions. The removal of off-odors is likewise of importance, and these persist in the various fractions to much the same degree as the color bodies.

The increasing use of glycerine by the food industries has stressed the importance of the removal of both color and odor from the grades used for such purposes. For other grades, such as Dynamite and Yellow Distilled, the color and odor requirements are not so critical but are defined by the specifications in each case. In order to meet the requirements of U.S.P. and extra quality grades it is usually necessary to treat the fractions going to these products to remove the last traces of color and off-odor. Sometimes it is

necessary to treat other fractions to improve them in these respects. The bleaching may be accomplished most readily by the use of activated carbon.

To avoid contamination of the product all equipment coming into contact with the bleached glycerine should be preferably nickel or stainless steel. However mild steel and iron are most commonly used in this service with good results.

The amount of activated carbon needed is dependent upon the quality of the glycerine being bleached, or the degree of color removal desired, and the activity of the carbon. Normally only a fraction of 1% is used and seldom over 2%. A smaller quantity of diatomaceous earth is ordinarily used as a filter aid. In plant practice the amount of carbon to be added is determined on the basis of past experience and judgment. Active carbon and filter aid are added to the glycerine in the bleach tank at a temperature of 165 to 175°F., are mixed for one or two hours, and then filtered. It is best not to exceed these temperatures in order to avoid developing color in the glycerine during mixing. On the other hand, glycerine does not filter readily below 160°F. so the bleaching is usually carried on in the range indicated.

Brant (6) describes a method of treatment with hydrogen peroxide for the removal of odorous substance from glycerine intended for the more critical uses. This method is distinguished from the conventional practice by the employment of lower temperatures, longer time of contact, and the use of small quantities of hydrogen peroxide. The product is described as of improved purity in that it will not develop color or off-odor under more critical conditions.

### The Purification of Glycerine by Ion Exchange

In May 1951 the first commercial ion-exchange (7) unit for the purification of soap-lye crude glycerine was put into successful operation at the new Lever Brothers Company plant at Los Angeles. This unit was designed by the Illinois Water Treatment Company of Rockford, Ill., and was fabricated and installed under their supervision.

Because sodium chloride comprises the bulk of the impurity which must be removed from crude glycerine in the purification process, ion-exchange has for some years been recognized as a means of accomplishing this end. Low capacity ion-exchange resins and high operating costs have heretofore made such a process economically inferior to conventional distillation methods. This was especially true in the purification of soap-lye crudes, which are high in salt content. The development of high capacity synthetic resins during the past few years has changed this picture however, and a point has been reached where it appears economically sound to instal ion-exchangers in a new plant instead of stills.

Preliminary investigational work on the purification of soap-lye crude glycerine by ion-exchange was an outgrowth of experiments made on saponification crude. Experiments were carried out on both laboratory and pilot-plant scale during 1949 and 1950 at the Ilco Laboratories in Rockford, Ill. In spite of the fact that the deionization of crude glycerine required dilution of the crude and reconcentration of the product, pilot-plant findings indicated that the process possessed a number of advantages over the conventional distillation method. Most important of these

were low capital investment, economy of operation, and exceptionally high product quality.

The ion-exchanger, which was installed at Los Angeles (Figure 7), is a four-stage unit, consisting of three pairs of cation anion exchangers and a mixed-bed, making a total of seven vessels, which are arranged in series. Each of the primary exchangers has

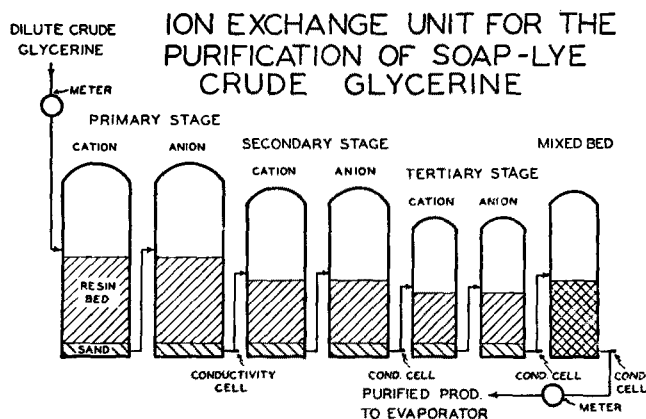


FIG. 7.

4,460-gal. capacity and contains approximately 330 cu. ft. of resin. Each of the secondary vessels has 920-gal. capacity and contains 66 cu. ft. of resin. Each of the tertiary units has 206-gal. capacity and contains 12 cu. ft. of resin. The mixed-bed has a capacity of 350 gal. and contains 8 cu. ft. of cation-exchange resin and 16 cu. ft. of anion exchange resin. In each of the first six exchangers the resin is supported by a bed of graded gravel.

All the exchanger vessels are of rubber-lined steel construction, built to withstand pressure. They are cylindrical in shape and sized in such a manner that all will become exhausted and require regeneration at approximately the same time.

Influent lines to the cation exchangers are for dilute glycerine, raw water, dilute sulfuric acid regenerant, and compressed air. Effluent lines are for the dilute product, clean and dirty water recovery, and waste to the sump. The anion exchangers are similarly equipped except that treated or softened water is used in place of raw water and dilute sodium hydroxide is used for regeneration instead of acid.

Radial-type distributors are located at the top, center, and bottom of each vessel. These handle the flow of liquid into and out of the tanks and are for the purposes of reducing turbulence and channeling.

Five different synthetic resins are employed in the unit. The choice and location of each in the system are based upon particular exchange and adsorption characteristics. For example, the primary cation exchanger, into which is first introduced the dilute crude glycerine, contains a high capacity resin of the sulfonic-acid type. The primary anion exchanger contains a weak-base, phenol formaldehyde resin, which has excellent color adsorption characteristics.

The ion-exchange plant was designed to purify 26,600 lbs. of crude (82%) glycerine per day in two 12-hr. cycles, using 13,300 lbs. of crude per cycle. A cycle includes dilution and purification of a batch of glycerine and the regeneration and preparation of the resins for further use. The impurities to be removed



from crude glycerine are sodium chloride, sodium sulphate, small amounts of calcium and magnesium from the water, traces of fatty acids, and non-ionized color and odor bodies.

Because of the fact that all resin beds are kept covered with water between cycles, some additional dilution of the crude material takes place as the glycerol solution passes through each vessel. This dilution is kept at a minimum and is referred to as "sweetening on" when the dilute crude is being run into the system, displacing the water in the resin voids. Dilution at the end of a purification run, when glycerol solution is being displaced from the resin voids by water, is referred to as "sweetening off." The terms "sweetening on" and "sweetening off" were borrowed from the sugar industry.

Each 13,300-lb. batch of crude is diluted to approximately 25% glycerine in the dilution tank and pumped through a Hercules leaf-type of filter into the primary unit at a rate of 150 g.p.m.

In passing through the primary cation exchanger, a large percentage (approximately 80%) of the sodium ions is removed and replaced by hydrogen ions. The hydrochloric acid formed by the exchange reaction is removed in the primary anion exchanger as is the bulk of the color and odor bodies.

As soon as a batch has been put into the system and run until the liquid level in each exchanger is in adjustment, a few inches above the resin bed, the unit is "sweetened off" by introducing raw water into the Primary Cation Exchanger at 20 g.p.m. This hydraulically pushes the dilute glycerine solution out of the resin bed and through each of the ion-exchange vessels (Figure 8).

#### TYPICAL DEIONIZATION CYCLE FOR DILUTE SOAP-LYE CRUDE GLYCERINE

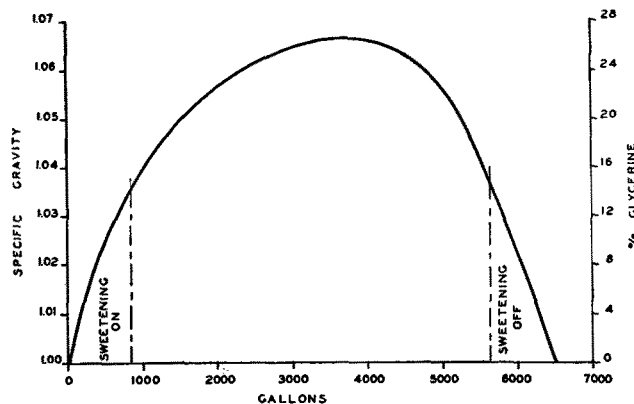


FIG. 8.

In "sweetening on" the mixed-bed, the effluent is discharged into the crude dilution tank for several minutes before glycerine appears in the product line. Dilute deionized glycerine is run into this tank until it reaches a concentration of approximately 15%, at which point it is run into the product storage tank. As the unit is "sweetened off," all solution containing less than 15% glycerine, is also run into the crude dilution tank. This glycerol solution is employed for diluting the next batch of crude.

By adjusting the quantity of glycerol solution returned to the crude dilution tank during "sweeten-

ing on" and "sweetening off," it is possible to eliminate the use of raw water for dilution. This improves efficiency and permits the purification of solutions containing up to 30% glycerine.

#### Regeneration

Regenerant solutions, 12% sulfuric acid for the cation exchange resins and 5% sodium hydroxide for the anion exchange resins, are run into the vessels at controlled rates.

Regeneration of all the anion resins is carried out simultaneously and at low flow rates to permit sufficient time for the reverse exchange reaction to take place. Sodium sulfate from the cation resins and sodium chloride from the anion resins are run to the waste sump together with the excess regenerant solutions.

The mixed bed is handled by a special technique involving classification of the resins during backwash, followed by simultaneous regeneration of the separated resins with alkali and acid.

After regeneration each bed is rinsed in parallel with fresh water, using raw water for cation exchangers and treated water for the anion exchangers. Washing is continued, downflow, at specific rates until the effluent acidity or alkalinity falls to a predetermined maximum figure. Following the parallel rinse is a series rinse, in which each pair of cation-anion exchangers is rinsed until the conductivity of the effluent from the anion exchangers reach specified limits. During the service part of the cycle, flow control is handled manually by the adjustment of throttle valves. Rotameters and disc-type fluid meters permit reasonably accurate control of flow rates through the system.

Liquid levels within the tanks are controlled by means of air pressure and manually operated valves. A pressure of approximately 40 p.s.i.g. is maintained on the dome of the primary cation exchanger, and each of the following vessels carried approximately 5 p.s.i.g. less than the one preceding it. Electrodes inside the vessels indicate high, normal, and low liquid levels by means of lights on a centrally located panel board.

In spite of an imposing array of manually operated valves in the system, the plant is run by a single operator. During the service cycle the one item which requires the most attention is the control of liquid levels by means of air pressure.

The deionized glycerine solution is evaporated under vacuum to 95-99% glycerol. The final product is exceptionally high in quality and does not require filtering or bleaching. It compares favorably with a high grade distilled glycerine.

#### The Purification of Crude Glycerine by Ion Exclusion

The ion exclusion process (8, 9) is a unit operation which utilizes ion exchange resins to separate solutes without the use of chemical regenerators. The separation is dependent upon the physical and chemical properties of the resin, and no net ion exchange takes place, that is, when an aqueous solution of two or more solutes is percolated through an ion exclusion column (which consists of ion exchange resins), a separation of the solutes occurs and they appear in separate fractions in the effluent. While ion exclusion is most applicable at higher ionic concentrations, in-

cluding those cases where ion exchange is prohibitive in cost, it is generally not feasible completely to remove all of the ionic material by ion exclusion. Therefore when complete deionization is desired, the bulk of the ionic material can be removed by ion exclusion and the remaining ionic material can be removed by conventional ion exchange.

Ion exclusion is a technique developed by the Dow Chemical Company, which utilizes ion exchange resins to effect the separation of water-soluble ionic salts from non-ionic glycerol material without the use of heat or regenerant chemicals other than water for elution. The polystyrene type ion exchange resins are in the form of small spherical beads. These beads contain a high percentage of water and are quite permeable. Due to the Donnan equilibrium effect, when these resin beads are placed in an aqueous solution of ionic and non-ionic materials, the ionic material tends to be more concentrated around the beads than inside the beads while the non-ionic material tends to have the same concentration within and without the beads. This difference in concentration within and surrounding the beads is the basic scientific fact upon which the ion exclusion process is based.

The simplest operation of the process consists of feeding a volume of an aqueous solution of ionic and non-ionic materials into a column filled with an ion exchange resin, following this with one or more volumes of rinse water. An aqueous solution of the ionic material comes out of the column first, followed by an aqueous solution of the non-ionic material. The separation may or may not be sharp and complete, and the effluent is more dilute than the feed solution when operating at low ionic concentrations, but the non-ionic can be concentrated with a high ionic concentration.

While almost any type of ion exchange resin may be used, Dow Chemical Company experiments have shown that the more strongly ionized resins give better results than those slightly ionized. It is also essential that the resin be in the same ionic form as

the ionic material being separated. In accord with the principle of ion exclusion the best resin would have the following properties:

The fixed ionic concentration inside the resin particles would be high.

The water content of the resin particles would be high to give a large capacity for the non-ionic component.

The diffusion rate would be high so that equilibrium would be rapidly attained.

The first requirement favors a high cross-linked resin, the second favors a low cross-linked resin, and the third implies either a low cross-linkage or small-particle size or both. Thus a compromise must be made, depending upon the requirements of a particular job.

An ion exclusion pilot plant, using the water-dome technique, has demonstrated that glycerol from soap lye crude can, on a practical basis, be separated from approximately 80% of its dissolved salts. There is an over-all loss of between 1.9% and 4.3% glycerol. The concentration of glycerol in the effluent product is approximately 15%, under average conditions, but varies with other factors, notably the feed concentration and recycle timing.

The product of ion exclusion, when further purified by a three-bed system of ion exchange followed by concentration, compares favorably with the product of both the distillation and ion exchange methods of purification.

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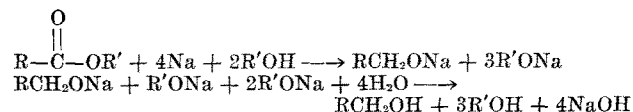
## Fatty Alcohols

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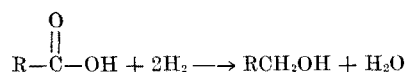
THROUGH AN OVERSIGHT, deliberate or accidental, nature has left a rather wide gap in the oxidative chain from hydrocarbon to fatty acid. Compared with the almost unlimited quantities of hydrocarbons and fatty acids available, the fatty alcohols are found in rather limited quantities, occurring in the free or combined state only in certain animal, vegetable, and mineral waxes. Even in these, certain members of the homologous series of fatty alcohols are conspicuously absent or present only in extremely small quantities.

As early as 1883 researchers were attempting to fill these gaps in the homologous series of fatty alcohols by tedious and many-step synthesis, which was complicated by undesirable side-reactions and very low yields. The first satisfactory laboratory synthesis of fatty alcohols, starting with available raw materials was discovered in 1903 by Bouveault and Blanc. Their procedure utilized the combined reductive ac-

tion of sodium and ethanol toward an ester grouping as follows:



The Bouveault and Blanc discovery remained a laboratory procedure for some 30 years. Near the end of this period, in the 1930's, a second and equally important reductive process for the preparation of fatty alcohols was discovered, namely, the hydrogenolysis process as follows:



This method involves the high temperature, high pressure reduction of fatty acids, esters, or salts with hydrogen in the presence of a copper chromite catalyst.