The Purification of Glycerin by Ion-Exchange[1]

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IN May, 1951, the first commercial ion-exchange unit for the purification of soap-lye crude glycerin was put into successful operation at the new Lever Brothers Company plant in Los Angeles, Calif. This unit was designed by the Illinois Water Treatment Company of Rockford, Illinois, and was fabricated and installed under their supervision. The purification capacity of the plant is 26,600 lbs. of crude glycerin per day.

Because of the fact that sodium chloride comprises the bulk of the impurity which must be removed from crude glycerin 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 install ion-exchangers in a new plant instead of stills.

Preliminary investigational work on the purification of soap-lye crude glycerin 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 Illco Laboratories in Rockford, Illinois. In spite of the fact that the deionization of crude glycerin 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.

Crude glycerin, as produced from soap lyes, is a viscous, amber-colored liquid which normally contains 82% glycerin and 10% ash;[2] the balance consists of moisture and other impurities. It is produced by the evaporation and desalting of treated soap lyes. The purification of crude glycerin is usually carried out batchwise in large stills under vacuum. The glycerol is steam distilled, and the vapors are condensed in fractions which represent C.P. (Chemically Pure) and H.G. (High Gravity) products. The C.P. glycerin is a colorless liquid which is concentrated under vacuum to the desired specific gravity, and finally bleached and filtered. Some of the extra quality grades of C.P. glycerin marketed today are double-distilled in order to meet the exacting color and odor specifications of buyers. The H.G. fraction contains more impurities than the C.P. fraction and is concentrated and marketed as a lower grade product.

Description of Plant and Process

Plant. The ion-exchanger, which was installed at Los Angeles, 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 4,460 gallons capacity and contains approximately 330 cubic feet of resin. Each of the secondary vessels has 920 gallons capacity and contains 66 cubic feet of resin. Each of the tertiary units has 206 gallons capacity and contains 12 cubic feet of resin. The mixed-bed has a capacity of 350 gallons and contains 8 cubic feet of cation-exchange resin and 16 cubic feet 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 and were 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. Each exchanger vessel is equipped with two glass observation ports located near the center of the side wall. These permit visual inspection of the resin surface and are used in connection with liquid-level control.

Influent lines to the cation exchangers are for dilute glycerin, 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 purpose of reducing turbulence and channeling.

All lines carrying partially deionized glycerin, acid, or alkali are rubber lined, and all valves in the system are of the Saunders patent type. Flow is controlled by Rotameters and disc-type fluid meters.

The crude glycerin dilution tank has a capacity of 12,000 gallons and is fabricated of steel. The dilute product tank, which serves only as a relay vessel, is fabricated of stainless-clad steel.

Waste from the plant, which includes spent regenerant solutions containing sodium sulphate, sodium chloride, sulphuric acid, sodium hydroxide, and organic color and odor bodies, is run into a 12,000-gallon sump. Dirty water, obtained from backwashing the resin beds, and rinse waters containing sulphuric acid and sodium hydroxide, are also run into this sump. Since more acid than alkali is used for regeneration, the waste regenerants do not neutralize one another in the sump and it is necessary to add soda ash before discharging the waste to the sewer.

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 glycerin, 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.

[1] Presented at the Fall Meeting of the American Oil Chemists' Society at Chicago, Ill., Oct. 8-10, 1951.

[2] The NaCl content of the ash is approximately 6%.

Process. The ion-exchange plant was designed to purify 26,000 lbs. of crude glycerin (82% glycerol) per day in two 12-hour cycles, using 13,300 lbs. of crude per cycle. A cycle includes dilution and purification of a batch of glycerin and the regeneration and preparation of the resins for further use. The impurities to be removed from crude glycerin are: sodium chloride, sodium sulphate, small amounts of calcium and magnesium from the water, traces of fatty acids, and nonionized 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 glycerin solution passes through each vessel. This dilution is kept at a minimum however 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 glycerin 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-pound batch of crude is diluted to approximately 25% glycerin in the dilution tank and pumped through a Hercules leaf-type filter into the primary unit at a rate of 150 g.p.m. The capacity of the two primary vessels, including the space above the resin beds, is greater than the volume of a single batch of dilute crude, and it is therefore possible to transfer an entire batch from the dilution tank to the primary unit at the high rate of 150 g.p.m.

As soon as a batch of dilute crude has been pumped into the unit, liquid levels in the primary vessels are adjusted by means of compressed air until normal operating levels are attained. During this adjustment period the following vessels are "sweetened on," and the effluent flow from the mixed-bed is controlled at a rate of 20 g.p.m. This rate is continued throughout the run and the subsequent "sweetening off" period.

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 a rate of 20 g.p.m. This hydraulically pushes the dilute glycerin solution out of the resin bed and through each of the following ion-exchange vessels.

In "sweetening on" the mixed-bed, the effluent is discharged into the crude dilution tank for several minutes before glycerin appears in the product line. Dilute deionized glycerin 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% glycerin is also run into the crude dilution tank. This glycerin solution is employed for diluting the next batch of crude.

By adjusting the quantity of glycerin solution returned to the crude dilution tank during "sweetening 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% glycerin.

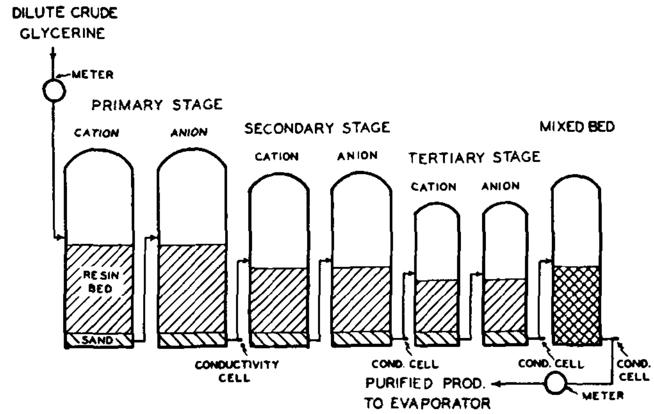

FIG. 1. Ion-exchange unit for the purification of soap-lye crude glycerine.

After the unit has been "sweetened off," all resin beds are backwashed to remove dirt and resin fines. Each vessel is backwashed at a preset rate, this rate being determined by the size of the particular vessel in question and the characteristics of the resin involved. The backwash effluent from each bessel is run to the waste sump for several minutes and then, to conserve water, to the cooling tower system.

Regeneration. After the backwash the liquid level in each tank is lowered to within a few inches of the resin bed, and regeneration is begun. Except for the mixed-bed, which requires special handling, regeneration is carried out downflow.

Regenerant solutions, 12% sulphuric acid for the cation exchange resins and 5% sodium hydroxide for the anion exchange resins, are run into the vessels at controlled rates. In practice, a quantity of reclaimed sulphuric acid is run through Primary Cation Exchanger before the introduction of the fresh 12% sulphuric acid solution. This reclaimed acid is from the prior regeneration of the Primary Cation Exchanger and represents a substantial amount of the fresh acid which was used for that regeneration.

In actual operation the reclaimed acid is pumped by means of a Duriron pump into the Primary Cation

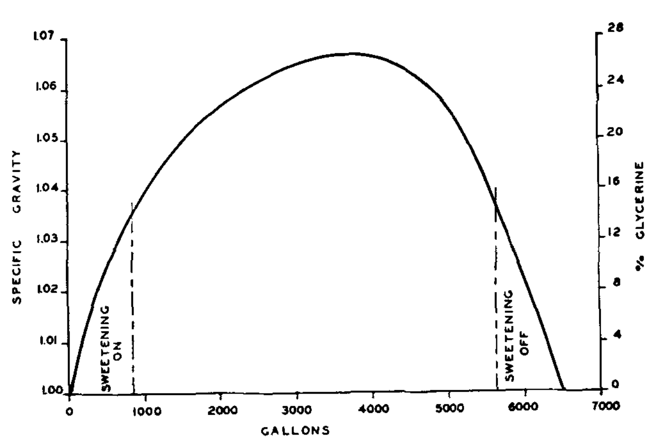

FIG. 2. Typical deionization cycle for dilute soap-lye crude glycerine.

Exchanger. When the reclaimed acid tank is empty, the pump automatically switches over to the fresh acid regenerant tank and pumps 12% sulphuric acid into the Primary Cation Exchanger. At the same time acid regenerant solution from the fresh acid tank is pumped to three gauge tanks which are located on an upper level. These are shut off automatically when filled and are for regeneration of the secondary, tertiary, and mixed-bed cation exchange resins.

Regeneration of all the anion resins is carried out simultaneously. A single pump supplies the feed for all anion exchangers, and the regenerant solution supplied to each is measured by disc-type fluid meters and controlled by impulse counters on panel board. These impulse counters are set to permit the flow of definite volumes of regenerant solution into each anion vessel and automatically stop flow when the meters count-out the volumes.

Regeneration is carried out 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. One exception to this is the fact that some of the used acid from the Primary Cation Exchanger is recovered and run into a reclaimed acid tank for use during the next cycle.

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. Since the anion-exchange resin is above the cation resin after separation, dilute caustic soda solution is run in at the top of the vessel and acid is run in at the bottom. The used regenerant solutions are removed through a drawoff line at the interface between the resins.

After regeneration each bed is rinsed in parallel with fresh water, using raw water for the 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 reaches specified limits. A considerable amount of the water used for the rinse operation is reclaimed and sent to the cooling tower system.

FIGURE 3
Analytical Data Showing Typical Double-Distilled Glycerin and Ion-Exchanged Glycerin

	Double-Distilled	Ion-Exchanged
Per cent glycerol	95.14	99.30
Per cent residue	0.0084	0.0070
Per cent ash	0.0034	0.0006
Per cent NaCl	0.0007	0.0005
Fatty acids and esters[a]	4.50	4.90

[a]This is a back-titration figure. Sample is treated with 5.0 ml. of 0.5 N. NaOH, and back-titrated with 0.5 N. HCl. The fatty acids and esters are expressed in terms of ml. of 0.5 N. HCl.

The mixed-bed is handled separately, with the anion resin being rinsed downflow with treated water and the cation resin being rinsed upflow with raw water. After rinsing, the mixed-bed resins are agitated and mixed by introducing air at the bottom of the vessel.

The ion-exchange cycle may be broken down to show the approximate time required for the various steps as follows:

	Hours
Dilution of crude and filtration	1½
"Sweeten on" (0 to 15% glycerin)	¾
Run (above 15% glycerin)	4
"Sweeten off" (15 to 0% glycerin)	¾
Regeneration of resins	5
Total	12

Control. 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 carries 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.

Panel Board. The panel board for the ion-exchange unit is equipped with a system for manually controlling liquid levels in each of the ion-exchange vessels, conductivity instruments for measuring the concentration and purity of solutions, recording specific gravity and conductivity instruments, and an automatic system for the preparation and dispensing of regenerant solutions. The board is also equipped with automatic timing and valve switching devices, and an alarm system which has both warning lights and an audible horn.

Product. The deionized glycerin 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 glycerin.

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