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## PRODUCTION OF GLYCERINE

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The invention relates to the production of glycerine, and it is particularly directed to an improvement in the method by which glycerine is synthesized by hydrolysis of an aqueous solution of the dichlorohydrin isomers 1,2-dichloro-3-hydroxypropane and 1,3-dichloro - 2 - hydroxypropane.

It is known that glycerine can be synthesized from allyl chloride by a number of methods. In one such method the allyl chloride is chlorinated to trichloropropane which is then hydrolyzed, though with difficulty, to glycerine. A second process involves the hydrolysis of allyl chloride to allyl alcohol, followed by chlorohydrination of the alcohol to various monochlorohydrins which are then hydrolyzed to glycerine. This is a relatively straight-forward and easy process since the allyl alcohol is water soluble and can be readily chlorohydrinated in relatively concentrated solution without excessive by-product formation.

The present invention is concerned with still a third method which involves the chlorohydrination of allyl chloride in aqueous solution to the dichlorohydrin isomers. The latter are then hydrolyzed to glycerine, following which the water present in the solution is evaporated and the remaining glycerine freed of its salt content. This method is considerably more difficult than that which proceeds through allyl alcohol because of the low water solubility of allyl chloride. Chlorohydrination of such materials has shown that the desired reaction takes place only in the aqueous phase, whereas the reactions occurring in any water insoluble phase present lead to the formation of water-insoluble by-products. For this reason the practice has been to employ relatively dilute solutions in order to minimize the amount of allyl chloride not dissolved in the water phase and thereby reduce the occurrence of side reactions. Further, a certain amount of by-product formation takes place in the aqueous phase, and it has been found that such reactions can also be minimized as the dilution is immersed. While both of these factors favor the use of increasingly dilute reaction solutions, the presence of additional water becomes a serious drawback when it becomes necessary to recover the glycerine, for all the water present in the system must then be removed by evaporation. This evaporation procedure is not only expensive but also serves to effectively limit the amount of glycerine which can be produced from a given plant unit, for once a given installation is complete there is usually no way in which to expand the capacity of the unit without providing

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additional evaporating equipment. Accordingly, the practice has been to strike a balance between the abnormally dilute dichlorohydrin solutions which are theoretically desired from the product yield standpoint and the more concentrated solutions which present a smaller load on the evaporating units.

It is a general object of the present invention to provide an improved method for synthesizing glycerine by hydrolysis of an aqueous solution of chlorohydrin isomers. A more particular object is to provide a method whereby the amount of water present in the latter solution can be reduced by inexpensive means, thereby decreasing the load which is subsequently placed on the glycerine evaporating units. A further object is to provide a method for decreasing said load even when the dilution of the dichlorohydrin solution is increased. Still another object is to provide a method for removing part of the salt formed prior to the final glycerine concentration step. The nature of other objects of the invention will be apparent from a consideration of the following description.

It is my discovery that the foregoing objects are attained by diverting a portion of the aqueous dichlorohydrin solution, as obtained by reaction of allyl chloride with chlorine, through a heated reaction vessel wherein the dichlorohydrin isomers present in said diverted portion are converted to epichlorohydrin, distilling off the epichlorohydrin from said vessel and combining it with the remaining dichlorohydrin solution, and hydrolyzing the chlorohydrins in the resulting solution to glycerine.

The glycerine solutions heretofore obtained by hydrolysis of the conventional dichlorohydrin solutions contain from about 2.5 to 5% by weight of glycerine, together with from about 6 to 9% salt. However, by converting a portion of the dichlorohydrin to epichlorohydrin, it is possible to provide glycerine solutions which contain as much as 10 to 15% glycerine, thereby greatly reducing the load placed on the glycerine evaporating units. Further, since the salt formed on hydrolysis of the diverted dichlorohydrins to epichlorohydrin is not removed with the epichlorohydrin but is discharged as bottoms from the epichlorohydrin distillation unit along with most of the water introduced therein, the glycerine evaporating unit is thus freed of a considerable portion of the salt which otherwise would be present therein. While not definitely understood, it is perhaps for this reason that the glycerine prepared by the method of the present

invention is superior in quality to that which has heretofore been synthesized directly from the dichlorohydrin solution.

In carrying out the present invention, from about 20 to 75% of the crude aqueous stream from the dichlorohydrin reactor is diverted to the epichlorohydrin unit. As larger amounts than this are diverted, glycerine solutions of unduly high concentration are obtained. This is a disadvantage since polymer formation increases at such concentrations and thereby impairs the efficiency of the unit. On the other hand, no appreciable benefit is obtained by diverting less than about 20% of the dichlorohydrin solution to the epichlorohydrin unit. In the preferred practice of the invention from about 35 to 65% of the aqueous dichlorohydrin solution is passed through the epichlorohydrin unit. The dichlorohydrin isomers in the diverted stream portion are converted to epichlorohydrin in known manner by heating the solution in the presence of a suitable alkaline additive. At least 2 mole equivalents of said additive, as caustic or lime, for example, are added for each mole of dichlorohydrin present, and preferably there is employed an excess of from about 2 to 20% caustic over the amount theoretically required. One mole equivalent of the alkaline additive goes to neutralize the hydrogen chloride which is present in the solution in equimolar amount with the dichlorohydrin isomers, whereas the other mole equivalent of caustic is that required to convert the dichlorohydrins to epichlorohydrin. As an alternative procedure, the entire aqueous solution emerging from the dichlorohydrin reactor may be treated with alkaline additive in an amount sufficient to bring the solution to neutrality. When this method is employed, correspondingly smaller amounts of alkaline additive need be supplied in the epichlorohydrin unit as well as in the subsequent glycerine hydrolysis step.

While a number of procedures can be employed to convert the diverted dichlorohydrin portion to epichlorohydrin, good results have been obtained by passing the diverted solution, heated to a temperature of about 150 to 210° F., into the upper portion of a stripper unit along with the required amount of the caustic or other alkaline additive. The contents of the stripper are heated by live steam which is passed upwardly through the unit. The epichlorohydrin is distilled from the stripper and condensed to an aqueous solution whose concentration is determined by the amount of steam admitted to the unit. Thus, condensates may be obtained which contain from about 10 to 40% epichlorohydrin in those cases where no portion of the condensate is recycled to the stripper as reflux, though with reflux the concentration of the epichlorohydrin stream may be increased to 90% or more.

Once the epichlorohydrin formed from the diverted dichlorohydrin stream has been recovered by stripping or otherwise, it is combined with the undiverted dichlorohydrin solution to form a much more concentrated solution of the chlorohydrin glycerine precursors than would otherwise be obtained. This combined solution is then hydrolyzed to glycerine and the glycerine recovered from the resulting aqueous solution by a practice of known methods. Thus, the chlorohydrin solution, if not already neutralized, is brought to the neutral point by the addition of a suitable alkaline additive which preferably is caustic. In addition, at least one mole of caustic is added for each mole of epichlorohydrin present, and two moles of caustic are added for each mole of dichlorohydrin in the solution. If desired, a buffer, as sodium carbonate, can be added to maintain the solution in the desired pH range. As is the case in the hydrolysis of dichlorohydrin to epichlorohydrin, hydrolysis of the epichlorohydrin and dichlorohydrin to glycerine is effected at elevated temperatures, usually from about 175 to 225° F. Once the hydrolysis of the glycerine precursors is complete, the glycerine-containing solution is fed to evaporating units where the water and glycerine are distilled off, preferably in vacuo. The salt present in the solution precipitates out as the evaporation proceeds and is removed by centrifuging or other convenient method.

The present invention is illustrated by the following examples:

*Example I*

In this operation allyl chloride and chlorine are reacted in aqueous medium to produce a solution containing approximately 4% by weight dichlorohydrin isomers, 92% water and the balance impurities. In forming this solution allyl chloride and make-up water are continuously fed to the reactor in the proportion of 25 volumes of water for each volume of allyl chloride, the chlorine being supplied in substantially equimolar amounts with respect to the allyl chloride. Under these conditions, the conversion of allyl chloride to dichlorohydrin is approximately 88%. The aqueous dichlorohydrin product solution, which is continuously withdrawn from the reactor at a temperature of about 100° F., is brought to a pH of about 8 to 9 by addition of caustic and is then fed to a hydrolyzer wherein the temperature of the solution is maintained at about 200° F. and where additional quantities of caustic are added in the amount theoretically required to effect hydrolysis of the dichlorohydrin to glycerine. At the end of the hydrolysis period (approximately 5 hours) there is obtained a solution containing about 3% glycerine, 7% salt and 90% water.

In this operation there is employed the same dichlorohydrin solution and glycerine hydrolysis treatment as described in the preceding paragraph. Here, however, 50% of the aqueous dichlorohydrin solution (brought to neutrality by addition of caustic) is diverted through an epichlorohydrin unit. This unit comprises a conventional stripper column, operated without reflux, into which the diverted dichlorohydrin solution, heated to a temperature of about 200° F., is fed near the top of the column together with a 45% solution of caustic in about 5 to 10% excess over the equimolar amount theoretically required to hydrolyze the dichlorohydrin to epichlorohydrin. Live steam is introduced near the bottom of the column (bottoms temperature, 215° F.) in an amount sufficient to provide a vaporous stripper effluent containing about 33% epichlorohydrin and 65% water. The bottoms discharged from the stripper contain substantially all the water admitted with the dichlorohydrin solution, together with the salt formed in the column, the feed bottoms containing approximately 96.6% water, 3.2% salt, 0.1% glycerine and lesser amounts of various other compounds. The vaporous effluent from the stripper, on being condensed, is combined with the undiverted aqueous dichlorohydrin solution and the resulting solution of chlorohydrin glycerine precursors is hydrolyzed to glycerine by heating with caustic as

described above. The resulting glycerine solution is now found to contain approximately 5.3% glycerine, 8.3% salt and the balance substantially water. From this it will be observed that by diverting a portion of the dichlorohydrin solution through the epichlorohydrin unit, the concentration of the glycerine in the final product solution has been nearly doubled. Further, the quantity of salt present in the glycerine solution has been reduced by approximately one third.

*Example II*

The operations described in this example are conducted under the same conditions as those described in Example I above, except that here the ratio of water to allyl chloride in the dichlorohydrin reactor is increased from 25:1 to 37:1. This change in reaction conditions has the desirable effect of increasing to 91.5% the conversion of allyl chloride to dichlorohydrin isomers and results in a solution containing approximately 3.5% of said isomers. When this solution is hydrolyzed to glycerine without diverting any portion thereof through the epichlorohydrin unit, there is obtained a glycerine solution containing approximately 2.6% glycerine, 6.1% salt and the balance water. On the other hand, when 50% of the dichlorohydrin solution is diverted through an epichlorohydrin stripper, there is obtained a solution containing approximately 4.6% glycerine, 7.2% salt and the balance water. From this it will be observed that even though the dilution of the dichlorohydrin solution is increased to effect higher conversion of the allyl chloride to dichlorohydrin, the resulting glycerine solution contains a higher percentage of glycerine (4.6%) than is obtained when a 25:1 allyl chloride water ratio is used and no portion of the resulting dichlorohydrin solution is fed through the epichlorohydrin unit (3%).

In a companion operation wherein the portion of the dichlorohydrin solution diverted through the epichlorohydrin unit is raised from 50% to 65%, a glycerine solution is obtained which contains 6% glycerine, 8% salt and the balance water.

The percentages given herein are on a weight basis unless otherwise indicated.

The invention claimed is:

1. In a process wherein an aqueous solution of dichlorohydrin isomers is hydrolyzed to glycerine, the steps comprising diverting from about 20 to 75% of said solution through a unit wherein said dichlorohydrin isomers are converted to epichlorohydrin, combining the epichlorohydrin formed in said unit with the undiverted portion of said dichlorohydrin solution, and hydrolyzing the chlorohydrins present in the resulting solution to glycerine.



2. In a process wherein an aqueous solution of dichlorohydrin isomers is hydrolyzed to glycerine, the steps comprising diverting from about 20 to 75% of said solution through a unit wherein the diverted solution is heated in the presence of at least 2 mole equivalents of an alkaline additive for each mole of dichlorohydrin present to convert said isomers to epichlorohydrin, evaporating the epichlorohydrin from said unit and combining the same with the undiverted portion of said dichlorohydrin solution, and hydrolyzing the epichlorohydrin and dichlorohydrin isomers present in the resulting solution to glycerine.

3. The method of claim 2 wherein the epichlorohydrin-forming unit comprises a stripper column into an upper portion of which the diverted dichlorohydrin solution is introduced and from which substantially all the water present in said solution is discharged as bottoms together with the salt present in the column.

4. The process comprising reacting allyl chloride and chlorine in an aqueous reaction medium to form a solution of dichlorohydrin isomers, diverting from about 20 to 75% of said solution through a unit where, in the presence of heat and an alkaline additive, the dichlorohydrins present in the unit are converted to epichlorohydrin, evaporating the epichlorohydrin from the unit and combining the same with the remaining portion of the dichlorohydrin solution, and hydrolyzing the epichlorohydrin and dichlorohydrin isomers present in the resulting solution, in the presence of heat and an alkaline additive, to glycerine.

5. The method of claim 4 wherein the epichlorohydrin-forming unit comprises a stripper column into an upper portion of which the diverted dichlorohydrin solution is introduced and from which substantially all the water introduced with said solution is discharged as bottoms together with the salt present in the column.

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## REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

| Number | Name | Date |
|---|---|---|
| 1,477,113 | Essex et al. | Dec. 11, 1923 |
| 2,061,377 | Groll et al. | Nov. 10, 1936 |

OTHER REFERENCES

Karrer, Organic Chemistry, 3rd English edition, page 301. Published by Elsevier Publishing Co., Inc., New York, 1947.