PRODUCTION OF GLYCERINE

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This invention relates to the conversion of glycerine epoxides, that is, the 1-halo-2,3-epoxypropanes, to glycerine. It deals with an improved process for carrying out this hydrolysis whereby the formation of undesirable by-products is suppressed and high yields of glycerine are obtained in an economical and efficient manner.

A number of different methods have been proposed for synthesizing glycerine. The more successful of these methods depend upon the hydrolysis of mono- and dichlorohydrials. Aqueous metal hydroxide solutions, preferably buffered with a salt of a strong base and a weak acid such as sodium carbonate, are used as the hydrolyzing agent. All of the prior methods have disadvantages of one kind or another in commercial scale operation. By-product formation, especially the formation of higher molecular products such as polyglycerols, is a serious disadvantage. Not only is the yield of glycerine reduced thereby, but also recovery of the glycerine in a pure form may be rendered more difficult as a result. Excessive consumption of reagents and relatively slow reaction making necessary the use of large and expensive reactors are other drawbacks which frequently accompany the methods previously suggested. A further disadvantage of such methods is the need for operating with aqueous solutions of low concentration which makes it necessary to evaporate large amounts of water in order to recover the glycerine in usable form, thus increasing its cost.

It is an object of the present invention to avoid the foregoing disadvantages of prior methods of producing glycerine. Another object is the provision of an efficient method for producing glycerine from 1-halo-2,3-epoxypropanes. Still another object is the hydrolysis of 1-chloro-2,3-epoxypropane under conditions at which glycerine is produced in high yields and in relatively high concentrations which simplify its recovery. Further objects and advantages of the process of the invention will be apparent from the following description of some of the methods which are suitable for carrying it out.

In accordance with the invention, the foregoing and other objects are achieved by carrying out the hydrolysis of 1-halo-2,3-epoxypropanes by short contact at high temperature and pressure with aqueous inorganic carbonate salt solution. The reaction is carried out at a temperature of 130° C. to 200° C. and under pressure of carbon dioxide in the range of 100 to 500 p. s. i. g. for a time of about 5 to 20 minutes. Optimum temperature and residence time vary somewhat with the glycerine concentration of the final, completely hydrolyzed product, as can be seen from the following figures:

<table>
<thead>
<tr>
<th>Glycerine concentration (% weight)</th>
<th>5</th>
<th>10-15</th>
<th>20-25</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, °C</td>
<td>154-195</td>
<td>157-190</td>
<td>163-189</td>
</tr>
<tr>
<td>Residence time, minutes</td>
<td>9-15</td>
<td>7-9</td>
<td>6-10</td>
</tr>
</tbody>
</table>

Temperatures and residence times above these optimum ranges promote excessive polymer formation. Those below the optimum range lead to incomplete hydrolysis. Temperature and residence time are dependent variables. The optimum ranges given define the limits within which an adjustment of one variable with respect to the other will give the best yield. Usually residence time is controlled by the volume of the reactor and the product throughput required. Optimum yield is then obtained by adjustment of the reaction temperature.

By this method of operation virtually complete conversion of the 1-halo-2,3-epoxypropane can be achieved with very little by-product formation. The reaction can be carried out advantageously with haloepoxy-propane solutions of relatively high concentration. Advantageously, aqueous solutions containing about 15% to 30% by weight of 1-chloro-2,3-epoxypropane are used. In contrast with prior methods of operation, formation of high boiling materials at these high concentrations is very small in the new method. At these concentrations correspondingly concentrated solutions of glycerine are obtained, thus materially reducing the amount of water which must be evaporated in recovering the product.

In addition to improved glycerine yields, an important advantage of the new method over prior practice is the material improvement in alkali economy which it gives. Preferably the process is carried out with an amount of inorganic carbonate such that 2% to about 20%, most preferably about 15% to about 20%, in excess of the stoichiometric requirements remains after completion of the reaction. Smaller amounts of carbonate can be used but less complete hydrolysis usually results, especially when less than 10% excess is employed. Larger amounts of inorganic carbonate do not improve the yield of glycerine and increase the load on the salt removal facilities. The efficiency of inorganic carbonate utilization is further increased by operating with higher concentrations of 1-halo-2,3-epoxypropane. Thus, it has been found that, while maintaining the optimum 15% to 20% excess of sodium carbonate in the product, the consumption of sodium carbonate fell from 79 pounds to 71 pounds per hundred pounds of glycerine produced when the glycerine concentration was increased from 15% to 25% by weight in the effluent, other conditions being the same and within the previously indicated ranges. This unexpected improvement is believed to be possibly attributable to reduced solubility of non-glycerine precursors in the reaction media at higher concentrations with resulting reduced reactivity of these impurities with carbonate.

Carbonates such as sodium carbonate have been suggested as the equivalents of other basic agents such as sodium hydroxide, etc. in the hydrolysis of hydroxy haldes. They are not equivalents of such other bases in the hydrolysis of 1-halo-2,3-epoxypropanes, however, and such other bases cannot be substituted for the carbonates used in the present process without sacrifice of important advantages of the invention. To achieve the desired results, inorganic carbonate or bicarbonate salts or mixtures thereof, all of which are included in the term inorganic carbonate as used herein generally, must be employed as the essential hydrolyzing agent. The carbonate ion is an important factor responsible for reduced by-product formation as well as for the rapid catalysis of the hydrolysis and hydration reaction. The hydroxide from the reaction may also act as a catalyst as well as a buffer to prevent high pH, which promotes excessive polymer formation. This does not, of course, preclude the use of such minor amounts of other basic agents as
do not essentially alter the reaction or change it substan-
tially from that produced when inorganic carbonates are
used as the sole hydrating agent. Thus, for example, more
than about 10%–15% by weight of sodium hydrox-
ide in the total alkali fed leads to undesirably increased
polymerization. The carbonate may be advantage-
ously produced by absorbing carbon dioxide liberated in
the reaction in caustic soda solution, for which purpose
a small excess of sodium hydroxide is desirable.

The preferred inorganic carbonate salts for use in
the process of the invention are the alkali metal car-
bonates and alkali metal bicarbonates. Sodium and
potassium carbonates are especially useful because of
their low cost and good solubility in the reaction medium.
Alkaline earth metal carbonates can be used but are less
desirable because of their low solubility.

The process has been found to be especially useful in
the hydrolysis of 1-chloro-2,3-epoxypropane to glycerine.
It has been used effectively, however, for the hydrolysis
of 1-bromo-2,3-epoxypropane and other 1-halo-2,3-
epoxypropanes can be similarly used. The starting 1-
halo-2,3-epoxypropane can be formed in the reaction
mixture from the corresponding dihalo hydroxypropanes.
It is only necessary in such cases to incorporate the and
by variation of sodium carbonate used by one-half mole for each
additional equivalent of halogen present. Mixtures of
dichlorohydrins and epichlorhydrin, for instance, those
described in Tymstra patent—U. S. 2,605,293, are suit-
ably converted to the new process.

Various procedures can be used in carrying out the
process. It can be conducted batchwise, intermittently,
or continuously. For the preferred continuous method
of operation one can use a reactor which may, if de-
sired, be filled with Raschig rings or other suitable in-
ert packing, or may be an unpacked vessel. The reactor
can be a horizontal vessel or of the vertical type, in
which case the halohydropyrrolyl or its precursors and
the aqueous sodium carbonate solution to be reacted therewith can be fed through the reactor in either upflow
or downflow. An unpacked reactor constructed of passes
or coils of piping offers advantages, particularly in pro-
viding good temperature control in the reaction. In such
a tubular reactor a gradual temperature rise as the re-
action progresses can be advantageously maintained.

More effective utilization of the inorganic carbonate is
obtained with such reactors, apparently due to minimized
backmixing and resulting suppression of side reactions
between the sodium carbonate and impurities in the feed.
Formation of undesirable high boiling by-products is
also inhibited in tubular type reactors through mini-
mized backmixing of glycerine with incompletely hy-
drolyzed reaction mixture. One can also use a com-
bination of a tubular reactor with a tank reactor in which
the initial stages of the reaction, corresponding to that
taking place in, say, about the first one-fifth to about one-
third of the total reactor volume in which a major portion
of the hydrolysis occurs, are carried out in heated re-
action tubes. The attached drawing is a schematic dia-
gram of one suitable reaction system of this type in which
the units are not drawn to scale.

In the drawing, 1 represents a storage tank for 1-halo-
2,3-epoxypropane or precipor, or mixtures thereof,
which is to be hydrolyzed to glycerine in accordance
with the present invention. This feed material is withdraw-

range of 130° C. to 200° C. as previously indicated.

The thus preheated mixture, under a pressure of 100 to 500
p. s. i. g. sufficient to maintain a liquid phase system, is
fed to reactor 10 containing a sufficient number of passes
of pipe 11 to provide about one-fourth of the total re-
actor volume at 130° C. to 200° C as previously indicated.

The thus preheated mixture is taken off by line 14, contain-
ing pressure reducing valve 15, to flash drum 16 in which carbon dioxide is separated and removed by line 17 from aqueous glycerine solution taken off by line 18. The excess sodium carbonate in the glycerine solution is neutralized with acid introduced by line 19 in neutralizer 20 from which the solution is taken off by line 21 and fed to evaporation and distillation units 22 and 23. The salt produced is removed conventionally and taken off by line 24, while the water and low boiling impurities are taken off by line 25 and the high boiling impurities by line 26. The pro-
duct glycerine is fed by line 27.

The carbon dioxide taken off by line 17 from the flash
drum 16, together with carbon dioxide removed by line
28 from neutralizer 20, is fed to absorber 29. In the
absorber the gaseous carbon dioxide is passed counter-
current to sodium hydroxide solution introduced by line
30. The resulting sodium carbonate solution is withdrawn
by line 31 and returned to the reaction by line 33 together with make-up sodium carbonate solution sup-
plied by line 32 in an amount sufficient to provide an equivalent of base per equivalent of reactive halogen in the feedstream from tank 1, and preferably about 5% to 20% in excess of such stoichiometric requirement.

By this method of operation, the amount of base re-
quired, i. e. sodium hydroxide supplied by line 30 and
sodium carbonate fed by line 32, is 20% to 35% less
than when the hydrolysis is carried out with buffered
sodium hydroxide, according to the best prior practice.
The amount of acid which must be fed by line 19 and
the amount of salt which must be removed from the glycerine are proportionately reduced. Also, the yield of
glycerine is significantly higher, especially due to the
reduced formation of undesirable high boiling products
which are only 1% to 4% of the amount previously pro-
duced.

The following examples illustrate these and other ad-
vantages of the new process as applied to the hydrolysis
of 1-chloro-2,3-epoxypropane.

**EXAMPLE 1**

1-chloro-2,3-epoxypropane (produced by steam strip-
ping an allyl chloride chlorohydrin product in the presence of a base), analyzing about 75% by weight 1-
chloro-2,3-epoxypropane, was used as feed to a pipe re-
actor constructed of 100 feet of 6-inch steel pipe ar-
ranged in a vertical stack of four horizontal passes in
series. The 1-chloro-2,3-epoxypropane and aqueous sodi-
um carbonate feed streams were mixed in a manifold
on the suction side of a reactor feed pump and charged
to the reactor at 150 p. s. i. g. Heat for the reaction
was supplied by direct injection of 175 p. s. i. g. steam
at a point about four feet downstream from the feed
inlet. Product from the reactor was reduced to atmos-
pheric pressure and the aqueous glycerine separated from
the carbon dioxide. The carbon dioxide was absorbed in
sodium hydroxide solution to produce sodium car-
bonate for further hydrolysis, and the aqueous glycerine
solution was neutralized, evaporated and distilled to
obtain pure, refined glycerine. The following are typical
results obtained in runs at different concentrations of
1-chloro-2,3-epoxypropane expressed as concentration of
equivalent glycerine in the reacted mixture, using the
reaction conditions in the ranges found to be optimum for these concentrations:

<table>
<thead>
<tr>
<th>Equivalent Glycerine Concentrations</th>
<th>5%</th>
<th>15%</th>
<th>25%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, °C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Residence Time, minutes</td>
<td>15-165</td>
<td>15-200</td>
<td>15-165</td>
</tr>
<tr>
<td>Excess NaOH in Feed, percent</td>
<td>5-8</td>
<td>5-10</td>
<td>5-8</td>
</tr>
<tr>
<td>Glycerine Comp. in Product, percent</td>
<td>5-10</td>
<td>5-10</td>
<td>5-10</td>
</tr>
<tr>
<td>Yield (Percent Glycerine Precursors Fed)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glycerine</td>
<td>95</td>
<td>95</td>
<td>95</td>
</tr>
<tr>
<td>Polymer w.</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
</tr>
</tbody>
</table>

The temperatures referred to herein and in the appended claims are the maximum temperatures attained during the reaction. Some reaction takes place at the lower temperatures at which the reactants are mixed and pumped to the reactor before the final heating to the specified reaction temperature is carried out.

The residence times reported in the foregoing table are calculated by dividing the reactor volume in gallons by the feed rate in gallons per minute. The actual liquid residence time in the reactor is somewhat lower due to the reactor volume occupied by the carbon dioxide liberated during the reaction.

**EXAMPLE II**

Tests of batch hydrolysis were made in a high pressure, stainless steel reactor provided with a high speed mixer and an internal heating coil. The reactor was charged with aqueous sodium carbonate solution which was heated, then the 1-chloro-2,3-epoxypropane (78.3% potential glycerine) was added and the reactor closed. The mixture at 80 °C-90 °C was then heated to the reaction temperature. When the evolved carbon dioxide has raised the pressure in the reactor to the desired level, the pressure was maintained constant for the remainder of the reaction period by releasing gas through a bleed-off valve to a scrubber in which the carbon dioxide was absorbed in 20% sodium hydroxide solution. The glycerine yield was determined from analyses of the feed stream, reactor product, reactor wash water, and the vent scrubber solution, after which hydroyzer product was worked up in the usual way for recovery of pure glycerine.

The following are the results of typical runs under different reaction conditions:

<table>
<thead>
<tr>
<th>Feed Composition (Percent w.)</th>
<th>Sodium Carbonate</th>
<th>Water</th>
<th>Stoichiometric Excess of NaOH</th>
<th>Maximum Reaction Temp. (°C)</th>
<th>Maximum Reaction Pressure (p.s.i.g.)</th>
<th>Reaction Time (min.)</th>
<th>Unhydrolyzed Glycerine (Percent w.)</th>
<th>High Boiling Product (Percent w.)</th>
<th>Glycerine Yield (Percent w.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Chloro-2,3-epoxypropane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.1</td>
<td>6.4</td>
<td>62.7</td>
<td>5</td>
<td>162</td>
<td>479</td>
<td>15</td>
<td>1.8</td>
<td>1.3</td>
<td>97.6</td>
</tr>
<tr>
<td>15.8</td>
<td>8.6</td>
<td>76.0</td>
<td>2</td>
<td>260</td>
<td>480</td>
<td>15</td>
<td>2.6</td>
<td>0.4</td>
<td>97.2</td>
</tr>
<tr>
<td>20.4</td>
<td>11.2</td>
<td>68.5</td>
<td>None</td>
<td>165</td>
<td>490</td>
<td>15</td>
<td>None</td>
<td>None</td>
<td>97.3</td>
</tr>
<tr>
<td>25.0</td>
<td>14.3</td>
<td>60.7</td>
<td>None</td>
<td>162</td>
<td>420</td>
<td>15</td>
<td>None</td>
<td>None</td>
<td>97.3</td>
</tr>
<tr>
<td>29.7</td>
<td>17.6</td>
<td>58.8</td>
<td>5</td>
<td>153</td>
<td>445</td>
<td>15</td>
<td>None</td>
<td>None</td>
<td>97.3</td>
</tr>
<tr>
<td>24.6</td>
<td>12.4</td>
<td>60.0</td>
<td>10</td>
<td>151</td>
<td>410</td>
<td>15</td>
<td>5.0</td>
<td>1.1</td>
<td>98.8</td>
</tr>
<tr>
<td>29.3</td>
<td>16.9</td>
<td>60.6</td>
<td>5</td>
<td>153</td>
<td>420</td>
<td>15</td>
<td>None</td>
<td>None</td>
<td>98.8</td>
</tr>
<tr>
<td>25.6</td>
<td>18.5</td>
<td>60.9</td>
<td>12</td>
<td>152</td>
<td>410</td>
<td>15</td>
<td>None</td>
<td>None</td>
<td>98.8</td>
</tr>
</tbody>
</table>

1 Reaction time is the total residence time in the reactor including the heat-up time.

**EXAMPLE IV**

The effect of changes in residence time upon the yield losses in hydrolyzing the impure 1-chloro-2,3-epoxypropane used in Example III is shown in the following table for tests made at temperatures of 157 °C to 177 °C with the pipe reactor described in Example I and the vertical tank reactor used in Example III.
I claim as my invention:  

1. A process for hydrolyzing a 1-halo-2,3-epoxypropane which comprises contacting the 1-halo-2,3-epoxypropane with an aqueous solution containing at least a stoichiometric amount of an inorganic carbonate of the group consisting of the alkali metal and alkaline earth metal carbonates, as the essential hydrolyzing agent at a temperature of 130° C. to 200° C. in the presence of carbon dioxide under a pressure in the range of 100 to 500 p. s. i. g. sufficient to maintain the reactants in the liquid phase for about 5 to 20 minutes, and recovering glycerine from the resulting reaction mixture.

2. A process in accordance with claim 1 wherein alkali metal carbonate hydrolyzing agent is used in an amount of about 2% to 20% in excess of the stoichiometric requirement for the hydrolysis.

3. A process in accordance with claim 1 wherein the reaction is carried out with an aqueous solution containing about 15% to 30% by weight of 1-chloro-2,3-epoxypropane.

4. A process for producing glycerine which comprises hydrolyzing 1-chloro-2,3-epoxypropane by contact with an aqueous solution containing at least a stoichiometric amount of sodium carbonate as the essential hydrolyzing agent at a temperature of 150° C. to 180° C. in the presence of carbon dioxide under a pressure in the range of 100 to 500 p. s. i. g. sufficient to maintain the reactants in the liquid phase for about 5 to 15 minutes.

5. A process in accordance with claim 4 wherein the reaction is carried out with about 10% to 20% excess of sodium carbonate above the stoichiometric requirement for hydrolysis of the starting material.

6. A process in accordance with claim 4 wherein the reaction is carried out with an aqueous solution containing about 15% to 30% by weight of 1-chloro-2,3-epoxypropane.

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<thead>
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<th>Issue Date</th>
</tr>
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<td></td>
</tr>
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</table>

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<thead>
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<th>Patent Number</th>
<th>Issuing Authority</th>
<th>Date</th>
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<tr>
<td>903,256</td>
<td>France</td>
<td>Sept. 28, 1945</td>
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