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M. A. YOUTZ
PREPARING GLYCOLS
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Fig. 1

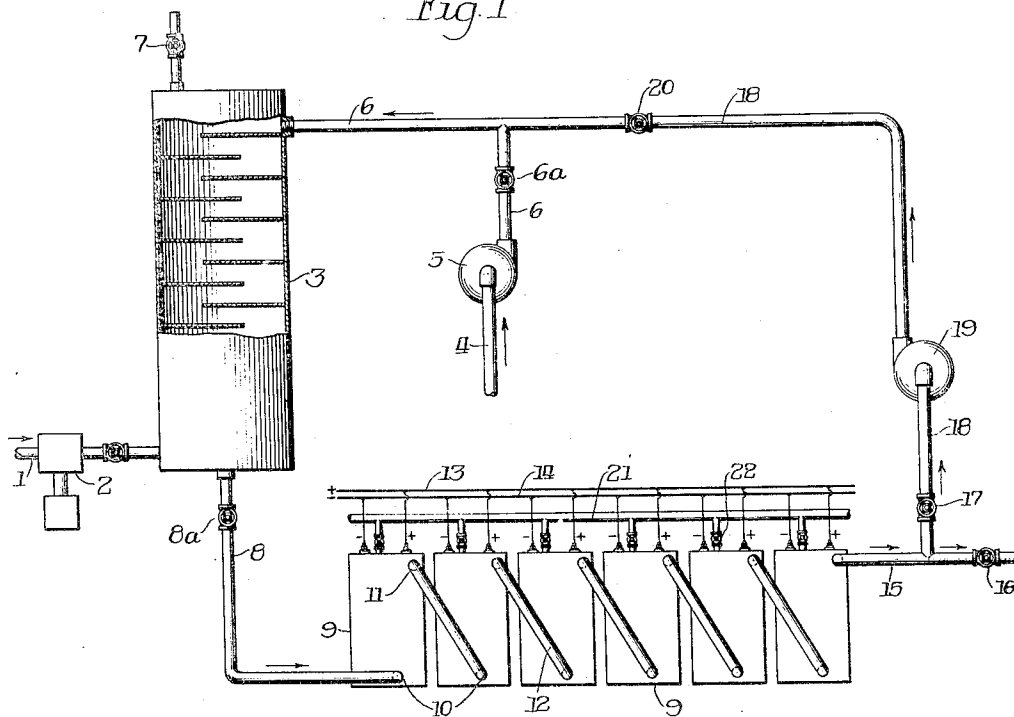
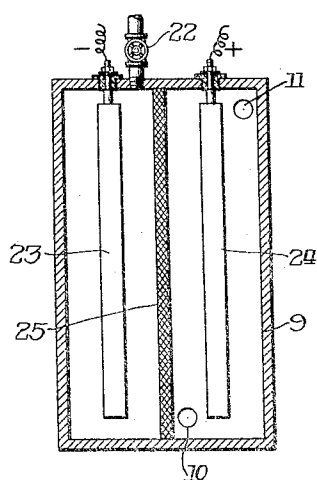


Fig. 2



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PREPARING GLYCOLS

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This invention relates to electrolytic processes of preparing glycols and it comprises a process wherein an aqueous solution of sodium hydroxide is saturated with an olefin gas and the resulting olefin solution electrolyzed; it further comprises processes wherein an aqueous solution of an appropriate electrolyte is saturated with an olefin gas under high pressure and the so saturated solution electrolyzed; and it additionally comprises processes wherein an olefin is dissolved under high pressure in a glycol solution containing an electrolyte and the olefin then converted to glycol electrolytically.

Most of the methods of preparing the glycols depend upon the hydrolysis of chlorhydrins by means of alkalis. Such processes involve either the substitution of a chlorine atom by hydroxyl or the conversion of chlorhydrins to olefin oxides and the hydration of the latter to glycols. Electrolytic processes wherein olefins are converted to chlorhydrins have been described. It has, for instance, been suggested to pass ethylene into a solution of sodium chloride undergoing electrolysis. Under properly controlled conditions it is possible to obtain ethylene chlorhydrin in this way. Suggestions are also found in the literature, patented and otherwise, that the glycols may be made directly from olefins by electrolytic processes. As far as I am aware, such processes have not proven very satisfactory.

I have now found that the electrolytic oxidation of olefins to glycols is improved when solutions of caustic soda are chosen as the electrolyte and I have also found that the process is greatly enhanced if relatively high pressures are used. Either of these newly discovered expedients materially improve the electrolytic oxidation. I find it best to use them together but electrolysis of a caustic soda solution through which the olefin is passed at pressures but slightly in excess of atmospheric leads to acceptable yields of glycols. So also, electrolysis of other suitable electrolytes saturated with the olefin under high pressure gives improved results but generally, I prefer to use high pressures and caustic soda solutions.

When using caustic soda solutions I may employ iron anode and cathode elements and this simplifies the design of the electrolytic cell. In the electrolysis of caustic soda solutions, hydrogen is liberated at the cathode as a result of the reaction between neutralized sodium ions and water so that the liquor surrounding the cathode is continuously replenished with caustic soda as a natural result of the process. Hydroxyl ions, migrating to the anode, are there neutralized and combine to form water and oxygen. In the presence of an olefin, however, the neutralized hydroxyl ions react therewith to form glycols. This means that in my process, I am, in effect, reacting olefin gas with water to form glycol and hydrogen.

In carrying out my process, I find it most advantageous to dissolve the olefin gas in the electrolyte under high pressure and pass the solution of olefin gas, still under high pressure, to one or more electrolytic cells. In the appended drawing, I have indicated the more general aspects of my process in semi-flow sheet form.

In the drawing,

Figure 1 represents an assembly of suitable apparatus, the various elements thereof being indicated more or less diagrammatically, and

Figure 2 shows in cross-section, a suitable type of cell I find useful.

Referring more particularly to Figure 1, olefin gas, which may consist of pure ethylene, propylene or butylene or mixtures thereof, or so-called still gases formed in petroleum refining operations, is conducted by pipe 1 to a pump 2 wherein it is compressed to a pressure of 20 to 200 atmospheres, roughly 300 to 3,000 pounds per square inch. The compressed gas enters the lower end of an absorption tower 3, provided with baffle plates as shown schematically. Other devices to insure efficient contact between liquids and gases can, of course, be used. An aqueous solution of an electrolyte coming from a source of supply through 4 is pumped into the top of the tower 3 by means of pump 5 and pipe 6 controlled by valve 6a. The pressure on the electrolyte must of course be above that within the tower.

A vent pipe 7 at the top of the tower permits undissolved gases to escape. Liquid collecting in the bottom of the tower will consist of an aqueous solution of electrolyte containing dissolved olefin gas under pressure. This solution is drawn from the tower by means of pipe 8 controlled by valve 8a and is passed to the electrolytic cells 9 shown as a bank of six. The outlets, 11, of each cell are connected to the inlets 10 of each succeeding cell. Suitable electrical connections to the cells are indicated by the bus bars 13 and 14. As shown, the saturated solution of olefin gas and electrolyte passes through the series of cells and leaves the last by pipe 15. The solution leaving the last cell consists of an aqueous solution of glycol and electrolyte and usually I pass this solution by valve 16 to suitable evaporators wherein the glycol is recovered. However, I sometimes find it advantageous to recycle a part or all of the crude glycol solution and this I do by by-passing a part of the crude glycol solution back to the top of the tower through pipe 18 controlled by valves 17 and 20 and the pump 19.

In Figure 2 I have shown a type of cell which I have found suitable for use in my process although there are a great many different types of cells which I can use. I do not restrict myself to any one type since cells for the electrolysis of caustic soda solution may take many forms.

The cell shown in Figure 2 consists of a steel container 9 having an inlet 10 and outlets 11. The electrode elements 23 and 24 may be of iron. They may be separated by a porous diaphragm 25, which is preferably of sufficient porosity to permit limited mixing of the solution in the two compartments, as well as equalization of pressure. However, a diaphragm is not essential to successful operation. The hydrogen which is evolved at the cathode 23 is conducted from the cells by vent pipe 21 controlled by valve 22 which is adjusted to permit the discharge of the hydrogen at about the same rate at which it is evolved at the cathode. Some olefin gas is carried along with the hydrogen, especially in the first cells, and I find it advantageous to pass the escaping gases to a tower wherein they be contacted with alcohol or other preferential solvents for the purpose of dissolving and recovering such olefins as are carried away with the hydrogen. Hydrogen itself is much less soluble in alcohol than are the olefins.

More specifically, and in one exemplification of my process, when I wish to make ethylene glycol, I compress the ethylene to a pressure of 20 to 200 atmospheres and pass the compressed ethylene into tower 3 wherein it comes into contact with a caustic soda solution of about 25% strength. There is nothing very critical about the strength of the electrolyte. Of course the higher the con-

centration thereof, the less electrical resistance will the cell have. But as the concentration of caustic soda solution is increased the solubility of ethylene therein decreases somewhat. A caustic soda solution of about 25% concentration gives me good electrical conductivity and about normal solubility of the ethylene in water under the prevailing temperature and pressure conditions. If the concentration of electrolyte is materially increased the resulting saving in electrical efficiency, because of lessened electrical resistance is overbalanced by the decreased solubility of the ethylene.

When saturating the electrolyte with ethylene or other olefin gas, and in the subsequent electrolysis, I find it best to keep the temperature at ordinary room temperature, say about 20° C.

I then pass the saturated solution of ethylene to the first electrolytic cell by way of valved pipe 8 and as the solution flows through the series of cells, the ethylene is converted therein to ethylene glycol. In the operation of the cells, the voltage should be about 2 to 2½ volts and the current density is about 20 amperes per square decimeter. Actually the current density may vary over a wide range without affecting the chemical reaction. From an operating standpoint it is desirable to keep down the current density to increase efficiency, but this is balanced against a lower capacity. The optimum value will vary with each installation.

The pressure is, of course, maintained on the solution during the passage thereof through the cells. As the ethylene becomes converted to glycol, the pressure changes somewhat with the absorption of ethylene and the evolution of hydrogen. Although the rate at which the solution flows through the cells may be controlled so that the solution leaving the last of the series is substantially olefin free, in the interest of higher efficiency it is found undesirable to carry the electrolysis this far in a single stage.

The solution leaving the last cell is conducted to a suitable evaporator wherein the glycol is recovered. A part or all of the crude glycol solution can be recirculated back to the tower 3. Since the electrolyte itself, that is, caustic soda, is being continuously regenerated at the cathodes during the electrolysis, no additional electrolyte need be added to the crude re-circulated solution. By re-circulating a part or all of the crude glycol, I can increase the concentration of the glycol in the crude liquor prior to sending it to the evaporators.

I find it most advantageous to work at relatively high pressures. At 200 atmospheres, for example, ethylene is soluble in water to the extent of about 28 grams per liter whereas under ordinary atmospheric pressure conditions and at about 20° C. ethylene is soluble

to the extent of about 0.14 grams per liter. In other words, when working at high pressures I am enabled to increase the amount of ethylene available for reaction purposes in any unit volume of solution 200 fold. Indeed, my process is essentially one occurring in a true liquid phase. The only ethylene I have present is that which is in the dissolved state. I avoid having gaseous ethylene present and this is in contradistinction to prior processes wherein gaseous ethylene has been bubbled under atmospheric pressure or pressures slightly above, past the anode of an electrolytic cell. When using pressures in the neighborhood of 200 atmospheres, the crude glycol solution leaving the cells contains upwards of 62 parts of glycol to 1000 parts of solution, in other words a concentration of about 6%. If the pressure is but 100 atmospheres, the glycol concentration in the crude solution amounts to about 3%. But even at pressures as low as 20 atmospheres, which I construe to be high, improved results are obtained. Working in a strictly liquid phase leads to high electrical efficiency and high yields of glycol with no by-products and this is undoubtedly due to the fact that at all times the ethylene or other olefin is substantially dissolved in water and I am not depending upon any reaction between a gas and a liquid reagent. Also since the concentration of dissolved ethylene is relatively very large compared to a low pressure process there is practically no tendency to further oxidize glycol to aldehydes, acids and CO₂. This is serious for low pressure processes and compels resort to extreme agitation to keep an excess of ethylene dissolved in the electrolyte in contact with the anode and to very low anode current densities to avoid local depletion of ethylene.

The process I have more specifically disclosed is continuous since ethylene gas or other olefin gas is continuously passed into the tower 3 and a solution thereof in the electrolyte is continuously withdrawn and continuously passed through the cells. Of course, if desired, the process can be rendered discontinuous and in this event I simply prepare a saturated solution of ethylene or other olefin in the electrolyte and pass the solution to a suitable cell wherein electrolysis is effected.

Throughout the process I prefer to work at temperatures not greatly in excess of ordinary room temperature, 20°-25° C. and it is somewhat advantageous to work at temperatures in the neighborhood of 10° C. since at the lower temperatures the solubility of the olefins in water is increased.

When using high pressures, electrolytes other than solutions of caustic soda may be used, so long as the electrolytic reaction of the cathode is one liberating oxygen, and improved results are had because of the high

pressures employed. However, I find that the best results are secured when high pressures are used in conjunction with caustic soda or other alkali metal hydroxide solutions.

When converting propylene and butylene, or mixtures thereof with ethylene or inert gases to the corresponding glycols, it is best not to exceed pressures at which there is any tendency for the higher olefins to liquefy. In the neighborhood of 11 atmospheres and 20° C. pure propylene condenses to a liquid and when using mixed olefin gases, pressures slightly below the liquefying pressures of the mixture are best used. However, some slight liquefaction of the olefin is not objectionable since when it liquefies the liquefied portion is more or less disseminated throughout the solution of electrolyte. Very high pressures far in excess of the liquefying pressure should be avoided if there is any tendency for the higher olefins to separate out in liquid layers. This tendency is not only dependent upon the actual pressures but is also determined somewhat by the concentration of the higher olefins in the gases being treated.

A single cell may of course be employed rather than a plurality of cells and material other than iron can be used for the electrode elements. Generally speaking, I find that what is good practice in the electrolysis of caustic soda solutions to form oxygen and hydrogen is good practice in the electrolysis of caustic soda solution saturated with olefin gas to form glycols and the particular arrangement of apparatus and design of cell is governed partly by prior practice with respect to the ordinary electrolysis of caustic soda solutions.

I find that my process is commercially practical even though the actual current efficiency may drop to 50% or even lower. This is because, in general, electrolytic processes are more satisfactory, in that high yields without the formation of undesirable by-products are obtainable. I have found no occasion to employ a catalyst of an oxygen carrier type although such catalysts have been proposed as adjuncts in electrolytic processes. Since, in my process, I am working substantially in the liquid phase, the reaction is enormously speeded up because of the higher concentration of olefin in the oxidation zone, and ordinarily no catalysts are necessary. However, I do not mean to exclude the use of catalysts from the scope of my invention should it be desirable to add one or more of such substances to the electrolyte prior to or during electrolysis.

What I claim is:

1. In the process of preparing glycols from olefins electrolytically, the step which comprises electrolyzing an alkali metal hydroxide

solution containing olefin dissolved therein under high pressure.

2. In the process of preparing ethylene glycol from olefins electrolytically, the step which comprises electrolyzing an alkali metal hydroxide solution containing ethylene dissolved therein under high pressure.

3. In the process of preparing ethylene glycol from ethylene electrolytically, the step which comprises electrolyzing a sodium hydroxide solution containing ethylene dissolved therein under a pressure of 20 to 200 atmospheres.

4. The process of preparing glycols which comprises electrolyzing a solution of an alkali metal hydroxide containing dissolved olefin.

5. The process of preparing ethylene glycol which comprises electrolyzing a solution of sodium hydroxide containing dissolved ethylene.

6. The process of preparing ethylene glycol which comprises electrolyzing a solution of sodium hydroxide and ethylene, the ethylene being substantially wholly dissolved in said solution.

7. The process of preparing glycols electrically which comprises saturating a solution of an appropriate electrolyte with an olefin under a pressure of at least 20 atmospheres so that substantially all of the olefin is in the dissolved state and any undissolved olefin is present in a liquefied condition, and the mixture is free of gaseous undissolved olefin, electrolyzing the so-formed mixture to convert the olefin therein to glycol, saturating at least a portion of the resulting glycol solution with additional quantities of olefin, and again electrolyzing.

8. The process of preparing glycols electrolytically which comprises saturating a solution of sodium hydroxide with an olefin to form a solution containing the olefin in a substantially wholly dissolved state, electrolyzing the so-formed solution to convert the olefin therein to glycol, saturating at least a portion of the resulting glycol solution with additional quantities of olefin and again electrolyzing.

9. The process of preparing ethylene glycol electrolytically which comprises saturating a solution of an appropriate electrolyte with ethylene under a pressure of at least 20 atmospheres so that substantially all of the ethylene is in the dissolved state and any undissolved olefin is present in a liquefied condition, and the solution is free of gaseous undissolved ethylene, electrolyzing the so-formed solution to convert the ethylene therein to glycol, saturating at least a portion of the resulting glycol solution with additional quantities of ethylene, and again electrolyzing.

10. The process of preparing ethylene glycol electrolytically which comprises saturating a solution of sodium hydroxide with

ethylene to form a solution containing the ethylene in a substantially wholly dissolved state, electrolyzing the so-formed solution to convert the ethylene therein to glycol, saturating at least a portion of the resulting glycol solution with additional quantities of ethylene, and again electrolyzing.

11. In the process of preparing glycols from olefins electrolytically, the steps which comprise dissolving an olefin in an aqueous solution of an appropriate electrolyte under a pressure of at least 20 atmospheres so that substantially all of the olefin is in the dissolved state and any undissolved olefin is present in a liquefied condition, and the solution is free of gaseous, undissolved olefin, and electrolyzing the so-prepared solution.

12. In the process of preparing glycols from olefins electrolytically, the steps which comprise dissolving ethylene in an aqueous solution of an appropriate electrolyte under a pressure of at least 20 atmospheres so that substantially all of the ethylene is in the dissolved state and the solution is free of gaseous, undissolved ethylene, and electrolyzing the so-prepared solution.

13. The process of preparing glycols from still gases electrolytically which comprises preparing an aqueous mixture of an appropriate electrolyte and still gas olefins wherein substantially all of the olefin is in the dissolved state and any undissolved olefin is in liquefied condition, and the solution is free of undissolved, gaseous olefin, and electrolyzing the so-prepared solution.

Signed this 28th day of January, 1930, at
Whiting, county of Lake, State of Indiana.
MERRILL A. YOUTZ.

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