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PROCESS FOR PRODUCING ALKYLENE GLYCOL

FIELD OF THE INVENTION

The present invention relates to a process for producing an alkylene glycol from an alkylene oxide. Alkylene glycols, especially ethylene glycol, are used as starting materials for resins and used in nonfreezing solutions, etc., and thus are industrially important compounds.

BACKGROUND OF THE INVENTION

The technique of hydrating alkylene oxides to produce alkylene glycols is known. In particular, the production of ethylene glycol by the hydration of ethylene oxide is being conducted at a large scale. However, in conventional techniques, undesirable by-products such as dialkylene glycols and trialkylene glycols are produced besides alkylene glycols. In order to inhibit the generation of such by-products to thereby heighten selectivity for alkylene glycols, water should be used in an amount as large as from 10 to 20 times that of the alkylene oxides. Use of such a large amount of water is undesirable from the standpoint of water removal at a purification step. Use of various catalysts for improving selectivity has been investigated as a means for eliminating the above problem, and many reports have been made thereon.

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Although it is known to use an acid or base alone as a catalyst, this technique is insufficient in selectivity improvement.

JP-A-51-127010 discloses the use of a combination of an organic base and carbon dioxide as a catalyst. (The term "JP-A" as used herein means an "unexamined published Japanese patent application".) As the organic base is used a tertiary amine.

JP-B-49-24448 discloses the use of a combination of an alkali halide or ammonium halide and carbon dioxide as a catalyst. (The term "JP-B" as used herein means an "examined Japanese patent publication".)

JP-B-60-45610 discloses the use of a molybdic acid salt as a catalyst.

JP-B-60-45611 discloses the use of a tungstic acid salt as a catalyst.

However, these conventional catalysts have a drawback that they dissolve in the reaction mixture and are hence difficult to recover therefrom. Several reports have hence been made on a technique for fixing the active ingredients of such conventional catalysts.

JP-B-60-56141 discloses the use of a combination of an anion-exchange resin which has undergone exchange for halogen anions and carbon dioxide as a catalyst.

JP-B-5-47528 discloses the use of a solid support, as a catalyst, which has an anion-exchanging ability and has

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undergone exchange for metal oxide anions such as molybdate ions, tungstate ions or vanadate ions. As the solid support is used an anion-exchange resin.

EP-A-741,683 discloses the use of a solid, as a catalyst, which has an anion-exchanging ability and has undergone exchange for hydrogencarbonate ions, hydrogensulfite ions, carboxylate ions or the like. As the solid is used an anion-exchange resin.

However, anion-exchange resins generally have low heat resistance, and the conventional catalysts each based on an anion-exchange resin do not necessarily have a sufficient catalytic life.

SUMMARY OF THE INVENTION

Accordingly, an object of the present invention is to provide a catalyst which has a prolonged catalytic life and is capable of yielding an alkylene glycol with a high selectivity.

Other objects and effects of the present invention will become apparent from the following description.

The above objectives of the present invention have been achieved by providing:

a process for producing an alkylene glycol which comprises a step of reacting an alkylene oxide with water in the presence of a catalyst,

wherein the catalyst comprises an anion-exchange resin comprising:

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a polymer of a vinylaromatic compound as a substrate; and

quaternary ammonium groups each bonded to the respective aromatic groups of the polymer substrate via a connecting group having a chain length of three or more atoms.

By the use of the above catalyst, the production of alkylene glycol can be conducted with high selectivity over a long period of time.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is described in detail below.

In the present invention, an anion-exchange resin having a structure comprising a polymer of a vinylaromatic compound as a substrate and a quaternary ammonium group bonded to each of aromatic groups of the polymer via a connecting group having a chain length of three or more atoms is used as a catalyst.

The substrate basically has the structure of a polymer of a monovinylaromatic compound, e.g., styrene, vinyltoluene, ethylvinylbenzene or vinylnaphthalene. It preferably has the structure of a crosslinked copolymer formed from such a monovinyl compound and a small proportion of a polyvinyl compound used as a crosslinking agent, e.g., divinylbenzene, divinyltoluene, divinylnaphthalene or ethylene glycol dimethacrylate. In particular, the structure

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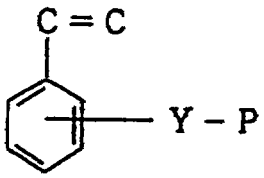
of a crosslinked copolymer formed from styrene and a small proportion of divinylbenzene is preferred.

The connecting group which bonds a quaternary ammonium group to the substrate should have a chain length of three or more atoms. The skeleton of the connecting group generally composed of carbon atoms or a combination of a carbon atom and an oxygen atom.

The anion-exchange resin having such a structure can be produced by copolymerizing a monovinylaromatic compound such as those enumerated above, which is represented by the following general formula (III), with a monovinylaromatic compound having a substituent which contains at the terminal thereof an labile member, such as a halogen atom (e.g., chlorine, bromine or iodine) or a tosyl group, and with a polyvinyl compound such as those enumerated above, and then reacting the resultant copolymer with a tertiary amine.



(III)

In the above formula (III), Y is a bivalent group having a chain length of three or more atoms; P represents a labile member present at the terminal of Y; and the benzene ring may have one or more substituents and may be a condensed aromatic ring.

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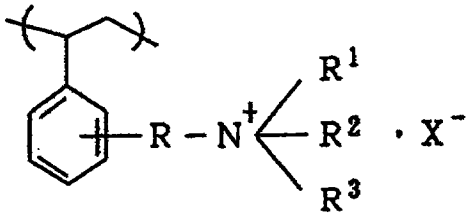
A preferred example of the anion-exchange resin for use in the present invention has a structural unit represented by the following general formula (I):



(I)

In the above formula (I), R represents an alkylene group having from 3 to 10, preferably from 3 to 6 carbon atoms, which group may contain a cyclic hydrocarbon group anywhere in the alkylene chain and may have one or more alkyl groups as substituents; R^1 to R^3 each represents an alkyl or alkanol group having from 1 to 4 carbon atoms; and X^- represents an anion; provided that the benzene ring may be substituted with one or more substituents selected from alkyl groups (e.g., those having 1 to 4 carbon atoms) and halogen atoms and may be a condensed aromatic ring (e.g., a naphthalene or anthracene ring).

Typical examples of the alkylene group represented by R include n-propylene, 1-alkyl-n-propylene groups, 2-alkyl-n-propylene groups, 3-alkyl-n-propylene groups, n-butylene, 1-alkyl-n-butylene groups, 2-alkyl-n-butylene groups, 3-alkyl-n-butylene groups, 4-alkyl-n-butylene groups, n-pentylene, 1-alkyl-n-pentylene groups, 2-alkyl-n-pentylene groups, 3-alkyl-n-pentylene groups, 4-alkyl-n-pentylene groups, 5-

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alkyl-n-pentylene groups, n-hexylene, 1-alkyl-n-hexylene groups, 2-alkyl-n-hexylene groups, 3-alkyl-n-hexylene groups, 4-alkyl-n-hexylene groups, 5-alkyl-n-hexylene groups, 6-alkyl-n-hexylene groups, 2,4-dialkyl-n-pentylene groups, 2,4-dialkyl-n-hexylene groups, 2,5-dialkyl-n-hexylene groups, and 3,5-dialkyl-n-hexylene groups. In the above, the term "n-alkylene" means a linear chain having a free univalent atom at each ends thereof, and the term "alkyl" means methyl or ethyl.

Typical examples of the alkyl or alkanol group represented by R^1 to R^3 include methyl, ethyl, n-propyl, isopropyl, n-butyl, s-butyl, t-butyl, isobutyl, 2-hydroxyethyl, 3-hydroxypropyl and 4-hydroxybutyl.

Examples of the anion represented by X^- include a hydroxyl ion, fluorine ion, chlorine ion, bromine ion, iodine ion, molybdate ion, tungstate ion, metavanadate ion, pyrovanadate ion, hydrogenpyrovanadate ion, hydrogensulfite ion, carboxylate ion and hydrogencarbonate ion. Of these, a molybdate ion, a tungstate ion, a metavanadate ion, a pyrovanadate ion, a hydrogenpyrovanadate ion, a carboxylate ion and a hydrogencarbonate ion are preferred. Two or more kinds of anions may be present. The anions can be easily exchanged by a commonly employed ion-exchange technique. It is also possible to conduct anion exchange during the reaction by using, as one of the reactants, water containing a desired anion. The anion-exchange resin having structural

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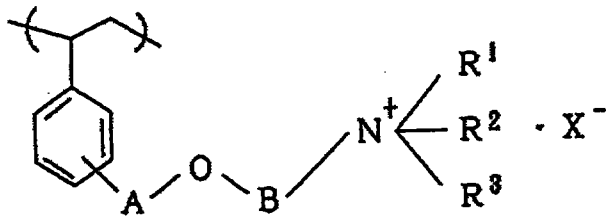
units represented by general formula (I) can be produced, for example, according to a method described in JP-A-4-349941.

Another preferred example of the anion-exchange resin for use in the present invention has a structural unit represented by the following general formula (II):



(II)

In the above formula (II), A represents an alkylene group having from 1 to 4 carbon atoms, which group may have one or more alkyl groups as substituents; B represents an alkylene group having from 1 to 8, preferably from 4 to 8 carbon atoms, which group may have one or more alkyl groups as substituents; and R^1 to R^3 and X^- have the same meanings as those in general formula (I); provided that the benzene ring may be substituted with one or more substituents selected from alkyl groups (e.g., those having from 1 to 4 carbon atoms) and halogen atoms and may be a condensed aromatic ring (e.g., a naphthalene or anthracene ring).

Examples of the alkylene group represented by A and B in general formula (II) include methylene, ethylene, and the same alkylene groups as those enumerated hereinabove as examples of R in general formula (I). The anion-exchange resin having structural units represented by formula (II) can

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be produced, for example, according to a method described in JP-A-7-289921.

In the present invention, an alkylene oxide is reacted with water in the presence of the anion-exchange resin described above, which comprises a vinylaromatic compound polymer as a substrate and quaternary ammonium groups each bonded thereto via a connecting group having a chain length of three or more atoms, to yield an alkylene glycol.

Examples of the alkylene oxide include aliphatic alkylene oxides such as ethylene oxide and propylene oxide and aromatic-alkylene oxides such as styrene oxide. Especially preferred of these are ethylene oxide and propylene oxide.

The reaction can also be conducted in the presence of carbon dioxide or an inert gas. The presence of carbon dioxide is preferred especially when the anion is a hydroxyl, chlorine, bromine or iodine ion. In the case of a hydroxyl ion, the presence of carbon dioxide can be considered as to be substantially equal to the use of an anion-exchange resin of the hydrogencarbonate ion type. Nitrogen, argon, helium, or the like can be used as the inert gas.

The reaction may be carried out batchwise, semi-batchwise, or continuously.

The molar ratio of water to an alkylene oxide, used as starting materials, is generally from 1/1 to 10/1,

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preferably from 1.2/1 to 6/1. If the proportion of water is below the lower limit, by-products such as dialkylene glycols and trialkylene glycols generate in an increased amount, resulting in a reduced selectivity for the target alkylene glycol. On the other hand, water proportions exceeding the upper limit are undesirable in that a larger reactor is necessitated and the removal of water from the reaction product in a purification system requires a large quantity of energy.

The reaction temperature is generally from 50 to 200°C, preferably from 60 to 160°C. The reaction pressure is generally from 0.1 to 5 MPa, preferably from 0.2 to 2 MPa.

The present invention will be described in detail with reference to the following Examples, but the invention should not be construed as being limited thereto.

In the Examples, the conversion and selectivity were calculated using the following equations.

Conversion of propylene oxide (%) = {(the number of moles of propylene oxide consumed)/(the number of moles of propylene oxide fed)} × 100

Selectivity for propylene glycol (%) = {(the number of moles of propylene glycol yielded)/(the number of moles of propylene oxide consumed)} × 100

Selectivity for dipropylene glycol (%) = {(the number of moles of dipropylene glycol yielded)/(the number of moles of propylene oxide consumed)} × 200

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Selectivity for tripropylene glycol (%) = {(the number of moles of tripropylene glycol yielded)/(the number of moles of propylene oxide consumed)} x 300

Conversion of ethylene oxide (%) = {(the number of moles of ethylene oxide consumed)/(the number of moles of ethylene oxide fed)} x 100

Selectivity for ethylene glycol (%) = {(the number of moles of ethylene glycol yielded)/(the number of moles of ethylene oxide consumed)} x 100

Selectivity for diethylene glycol (%) = {(the number of moles of diethylene glycol yielded)/(the number of moles of ethylene oxide consumed)} x 200

Selectivity for triethylene glycol (%) = {(the number of moles of triethylene glycol yielded)/(the number of moles of ethylene oxide consumed)} x 300

The following anion-exchange resins were used as catalysts.

Catalyst A:

An anion-exchange resin having a structural unit represented by the following formula (IV) (exchange capacity in Cl form, 1.27 meq/ml; water content, 45.7%) produced by suspension-polymerizing styrene having a 4-bromobutyl group with divinylbenzene in an aqueous medium to obtain a crosslinked copolymer, reacting the thus obtained copolymer with trimethylamine to obtain an anion-exchange resin in quaternary ammonium form, and then treating the resin with an

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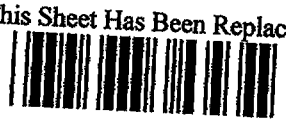
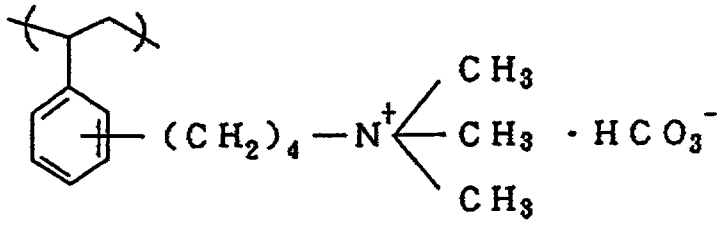


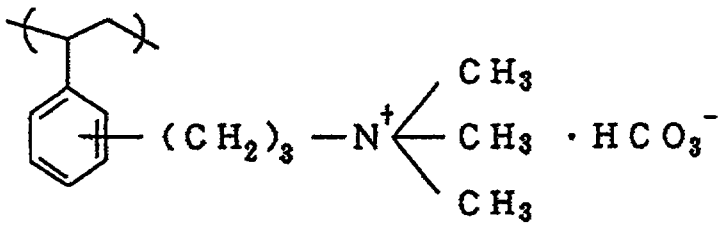
aqueous sodium hydrogencarbonate solution to convert the same to the hydrogencarbonate form.



(IV)

Catalyst B:

An anion-exchange resin having a structural unit represented by the following formula (V) (exchange capacity in Cl form, 1.10 meq/ml; water content, 52.7%) produced by suspension-polymerizing styrene having a 3-bromopropyl group with divinylbenzene in an aqueous medium to obtain a crosslinked copolymer and subjecting the thus obtained copolymer to the same treatments as in the production of Catalyst A.



(V)

Catalyst C:

An anion-exchange resin having a structural unit represented by the following formula (VI) (exchange capacity in Cl form, 1.21 meq/ml; water content, 46.6%) produced by suspension-polymerizing styrene having a 4-bromobutoxymethyl

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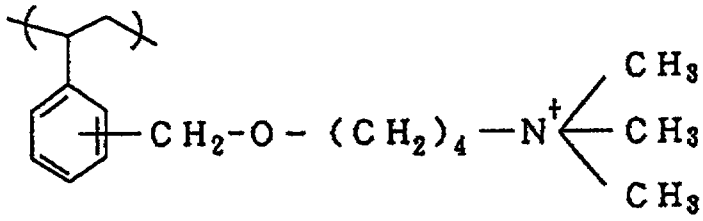
group with divinylbenzene in an aqueous medium to obtain a crosslinked copolymer and subjecting the thus obtained copolymer to the same treatments as in the production of Catalyst A.



(VI)

Catalyst D:

An anion-exchange resin produced by subjecting DIAION SA10A to ion exchange with an aqueous sodium hydrogencarbonate solution. (The DIAION, a trademark of Mitsubishi Chemical Corp., is manufactured by Mitsubishi Chemical Corp., which has a structure composed of a styrene/divinylbenzene copolymer skeleton and trimethylaminomethyl groups bonded thereto, and has an exchange capacity in Cl form of 1.26 meq/ml and a water content of 45%.)

Catalyst E:

An anion-exchange resin produced by subjecting LEWATIT M511WS to ion exchange with an aqueous sodium hydrogencarbonate solution. (The LEWATIT is manufactured by Bayer Ltd., which has an exchange capacity of 1.4 eq/liter and a water content of from 43 to 49%.)

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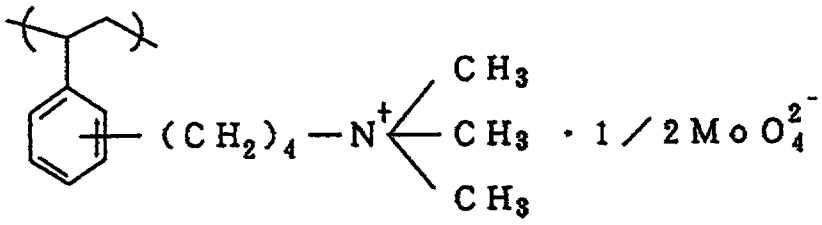
Catalyst F:

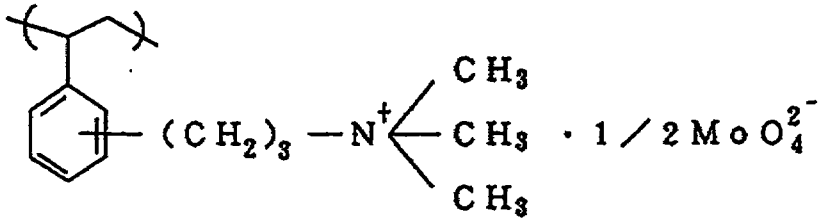
An anion-exchange resin having a structural unit represented by the following formula (VII) produced by subjecting the anion-exchange resin obtained in the course of the production of Catalyst A to ion exchange with an aqueous sodium molybdate solution.



(VII)

Catalyst G:

An anion-exchange resin having structural units represented by the following formula (VIII) produced by subjecting the anion-exchange resin obtained in the course of the production of Catalyst B to ion exchange with an aqueous sodium molybdate solution.



(VIII)

Catalyst H:

An anion-exchange resin having structural units represented by the following formula (IX) produced by subjecting the anion-exchange resin obtained in the course of

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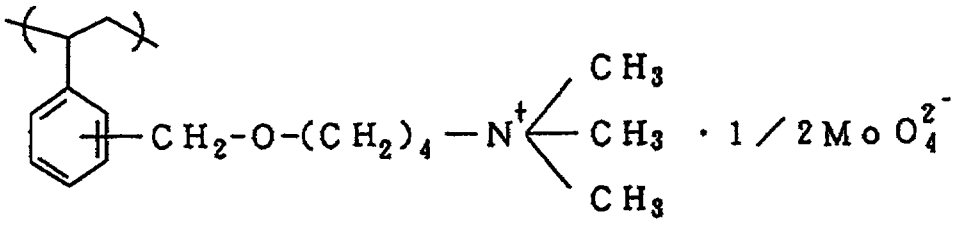
the production of Catalyst C to ion exchange with an aqueous sodium molybdate solution.



(IX)

Catalyst I:

An anion-exchange resin produced by subjecting DIAION SA10A to ion exchange with an aqueous sodium molybdate solution.

Catalyst J:

An anion-exchange resin produced by subjecting DOWEX MSA-1 to ion exchange with an aqueous sodium molybdate solution. (The DOWEX is manufactured by Dow Chemical Limited, which has an exchange capacity of 1.2 eq/liter and a water content of from 57 to 63%.)

EXAMPLE 1

Into an SUS autoclave having a capacity of 30 ml were introduced 2 g of the respective catalyst in a wet state, 5.4 g of water, and 8.7 g of propylene oxide. The autoclave was immersed in a 150°C oil bath to react the reactants for 1.5 hours with stirring. The reaction temperature was 140°C. The resultant reaction mixture was analyzed by gas chromatography. The results obtained are shown in Table 1.

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Table 1

Catalyst	A	B	C	D	E	F	G	H	I	J
Conversion of propylene oxide (%)	100	100	100	100	100	99.3	99.7	99.8	99.6	99.8
Selectivity for propylene glycol (%)	89.0	89.0	89.4	87.3	87.6	87.2	86.7	87.0	88.6	86.1
Selectivity for dipropylene glycol (%)	10.3	10.3	9.9	11.7	11.8	11.3	11.5	11.6	10.6	13.0
Selectivity for tripropylene glycol (%)	0.7	0.7	0.7	1.0	0.6	1.5	1.8	1.4	0.9	0.9

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EXAMPLE 2

Some of the catalysts used in Example 1 were washed with water and then used to carry out the same reaction as in Example 1 under the same conditions. This procedure was repeatedly conducted three times in total (the catalysts were washed each time before use). The results of the third reaction are shown in Table 2.

Table 2

Catalyst	A	B	C	D	E
Conversion of propylene oxide (%)	100	100	100	100	99.9
Selectivity for propylene glycol (%)	88.8	88.4	89.1	83.8	82.9
Selectivity for dipropylene glycol (%)	10.5	11.1	10.3	15.5	16.4
Selectivity for tripropylene glycol (%)	0.7	0.4	0.6	1.2	0.7

EXAMPLE 3

Into an SUS autoclave having a capacity of 30 ml were introduced 2 g of a catalyst in a wet state, 5.4 g of water, and 8.7 g of propylene oxide. The autoclave was immersed in a 150°C oil bath to react the reactants for 1.5 hours with stirring. Thereafter, the autoclave was kept being immersed in the 150°C oil bath for 48 hours.

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The catalyst was separated from the reaction mixture, washed with water, and then used to conduct the same reaction as in Example 1 under the same conditions. The results obtained are shown in Table 3.

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Table 3

Catalyst	A	B	C	D	E	F	G	H	I	J
Conversion of propylene oxide (%)	100	100	100	100	100	99.3	99.7	99.8	99.6	99.8
Selectivity for propylene glycol (%)	87.1	87.3	88.0	62.8	55.1	89.1	88.7	89.4	80.7	79.7
Selectivity for dipropylene glycol (%)	12.4	12.1	11.8	33.1	37.2	10.3	10.2	9.7	17.6	18.0
Selectivity for tripropylene glycol (%)	0.5	0.6	0.2	4.2	0.6	0.7	1.1	0.9	1.7	2.3

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EXAMPLE 4

Into an SUS autoclave having a capacity of 1500 ml were introduced 40 ml of the respective catalyst in a wet state, 270 g of water and 132 g of ethylene oxide. Catalyst A and D were respectively used as the catalyst. The autoclave was heated so as to maintain the reaction temperature at 120°C and the reactants were reacted for 2 hours with stirring. The resultant reaction mixture was analyzed by gas chromatography. The results obtained are shown in Table 4.

Table 4

Catalyst	A	D
Conversion of ethylene oxide (%)	100	100
Selectivity for ethylene glycol (%)	87.3	87.0
Selectivity for diethylene glycol (%)	12.0	12.3
Selectivity for triethylene glycol (%)	0.6	0.7

As is apparent from the foregoing results, the anion-exchange resin for use in the present invention, which comprises a substrate and quaternary ammonium groups each bonded thereto via a connecting group having a chain length of three or more atoms, yields an alkylene glycol with a high

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selectivity even after exposed to a high temperature over a long period of time.

While the invention has been described in detail and with reference to specific examples thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

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WHAT IS CLAIMED IS:

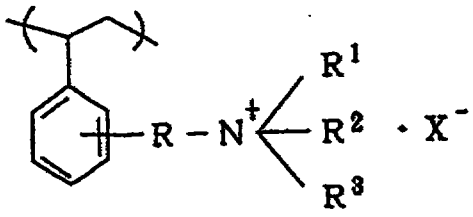
1. A process for producing an alkylene glycol which comprises a step of reacting an alkylene oxide with water in the presence of a catalyst,

wherein said catalyst comprises an anion-exchange resin comprising:

a polymer of a vinylaromatic compound as a substrate; and

quaternary ammonium groups each bonded to the respective aromatic groups of said polymer substrate via a connecting group having a chain length of three or more atoms.

2. The process according to claim 1, wherein said anion-exchange resin has a structural unit represented by the following general formula (I):



(I)

wherein R represents an alkylene group having from 3 to 10 carbon atoms, which group may contain a cyclic hydrocarbon group anywhere in the alkylene chain and may be substituted with an alkyl group; R^1 to R^3 each represents an alkyl or alkanol group having from 1 to 4 carbon atoms; and X^- represents an anion, provided that the benzene ring in the

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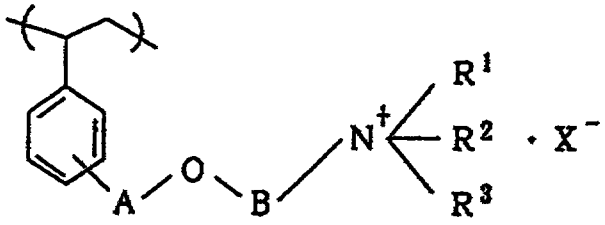
* C L M S *

formula (I) may be substituted with one or more substituents selected from alkyl groups and halogen atoms and may be a condensed aromatic ring.

3. The process according to claim 1, wherein said anion-exchange resin has a structural unit represented by the following general formula (II):



(II)

wherein A represents an alkylene group having from 1 to 4 carbon atoms, which group may be substituted with an alkyl group; B represents an alkylene group having from 1 to 8 carbon atoms, which group may be substituted with an alkyl group; R^1 to R^3 each represents an alkyl or alkanol group having from 1 to 4 carbon atoms; and X^- represents an anion, provided that the benzene ring in the formula (II) may be substituted with one or more substituents selected from alkyl groups and halogen atoms and may be a condensed aromatic ring.

4. The process according to claim 1, wherein said polymer substrate of the anion-exchange resin is a crosslinked copolymer of vinylaromatic compounds.

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* C L M S *

5. The process according to claim 4, wherein said polymer substrate is a crosslinked copolymer of styrene and divinylbenzene.

6. The process according to claim 1, wherein said alkylene oxide is ethylene oxide or propylene oxide.

7. The process according to claim 2, wherein said anion is a hydroxyl ion, a chlorine ion, a bromine ion, an iodine ion, a molybdate ion, a tungstate ion, a metavanadate ion, a pyrovanadate ion, a hydrogenpyrovanadate ion, a hydrogensulfite ion, a carboxylate ion or a hydrogencarbonate ion.

8. The process according to claim 7, wherein said anion is a molybdate ion, a tungstate ion, a metavanadate ion, a pyrovanadate ion, a hydrogenpyrovanadate ion, a carboxylate ion or a hydrogencarbonate ion.

9. The process according to claim 3, wherein said anion is a hydroxyl ion, a chlorine ion, a bromine ion, an iodine ion, a molybdate ion, a tungstate ion, a metavanadate ion, a pyrovanadate ion, a hydrogenpyrovanadate ion, a hydrogensulfite ion, a carboxylate ion or a hydrogencarbonate ion.

10. The process according to claim 9, wherein said anion is a molybdate ion, a tungstate ion, a metavanadate ion, a pyrovanadate ion, a hydrogenpyrovanadate ion, a carboxylate ion or a hydrogencarbonate ion.

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11. The process according to claim 1, wherein the reaction is conducted at a temperature of from 50 to 200°C.

12. The process according to claim 1, wherein the reaction is conducted at a pressure of from 0.1 to 5 MPa.

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