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(54) **Title:** METHOD FOR OBTAINING PROPYLENE OXIDE

(57) **Abstract:** An object the present invention is to provide a method for obtaining propylene oxide in which the content of acetaldehyde is reduced by enabling the removal of acetaldehyde. More specifically, the present invention provides a method for obtaining propylene oxide, which includes steps of: mixing a hydroxylamine compound in a reaction mass which is obtained by reacting both raw materials of (a) hydrogen peroxide, or hydrogen and oxygen, and (b) propylene in an acetonitrile-containing solvent in the presence of a catalyst, thereby entirely or partially converting acetaldehyde contained in the reaction mass into acetaldoxime, and then separating or removing the acetaldoxime from the reaction mass; and recovering the reaction mass obtained by the former step or propylene oxide existing in the reaction mass.



DESCRIPTION

Title of Invention

METHOD FOR OBTAINING PROPYLENE OXIDE

5 Technical Field

[0001]

The present invention relates to a method for obtaining propylene oxide.

10 Background Art

[0002]

Patent Document 1 specifically describes a method wherein in the process for the production of ethylene oxide, formaldehyde, which is produced as by-products in an aqueous solution, is converted into a corresponding salt by a reaction with a bisulfite of an alkali metal, such as sodium bisulfite, and then the corresponding salt is removed from the process by recovery and distillation of ethylene oxide, in Example 1 and Example 2 thereof.

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Citation List

[Patent Literature]

[0003]

Patent Literature 1: JP-A-7-330746

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Summary of the Invention

Technical Problem

[0004]

The patent document describes that the above-mentioned method is not applied to aldehydes other than formaldehyde, and the method is not necessarily satisfactory as a method of removing other aldehydes such as acetaldehyde. An object of the present invention is to provide a method for obtaining propylene oxide in which the content of acetaldehyde is reduced by enabling the removal of acetaldehyde.

Solution to Problem

[0005]

Under these circumstances, the present inventors have intensively studied, and thus leading to the following present invention.

Namely, the present invention includes:

1. A method for obtaining propylene oxide (hereinafter sometimes referred to as a first obtaining method of the present invention), which includes steps of:

mixing a hydroxylamine compound in a reaction mass which is obtained by reacting both raw materials (hereinafter both raw materials are sometimes referred collectively to as main raw materials) of (a) hydrogen peroxide, or hydrogen and oxygen, and (b) propylene in an acetonitrile-containing solvent in the presence of a

catalyst, thereby entirely or partially converting acetaldehyde contained in the reaction mass into acetaldoxime, and then separating or removing the acetaldoxime from the reaction mass; and

5 recovering the reaction mass obtained by the former step or propylene oxide existing in the reaction mass;

2. The method for obtaining propylene oxide according to the above item 1, wherein the separation/removal step is a step of mixing a hydroxylamine compound in the reaction
10 mass, which is obtained by feeding, as a liquid gas, a reaction mass obtained by reacting the both raw materials into a gas-liquid separator, and separating into a reaction mass as a liquid part and a gas as a gas part under a pressure which is the same as or lower than that obtained
15 in the reaction, thereby entirely or partially converting acetaldehyde contained in the reaction mass into acetaldoxime, and then separating or removing the acetaldoxime from the reaction mass;

3. The method for obtaining propylene oxide according to
20 the above item 1 or 2, wherein the hydroxylamine compound is hydroxylamine sulfate or hydroxylamine hydrochloride;

4. The method for obtaining propylene oxide according to the above item 1 or 2, wherein the separation/removal step and the recovery step are allowed to proceed
25 simultaneously;

5. The method for obtaining propylene oxide according to

the above item 4, wherein the separation/removal step and the recovery step are steps of distilling a reaction mass before removing acetaldoxime, and the distillation step includes a step of separating or removing by recovering a top liquid of a distillation column, which contains propylene oxide, from a top section of the column and also recovering a bottom liquid of the column, which contains acetaldoxime and acetonitrile, from a bottom section of the column;

6. A method for obtaining propylene oxide (hereinafter sometimes referred to as a second obtaining method of the present invention), which includes steps of:

recovering propylene oxide existing in a reaction mass which is obtained by reacting both raw materials

(hereinafter both raw materials are sometimes referred collectively to as main raw materials) of (a) hydrogen peroxide, or hydrogen and oxygen, and (b) propylene in an acetonitrile-containing solvent in the presence of a catalyst; and

mixing a hydroxylamine compound in the reaction mass obtained after recovering propylene oxide by the former step, thereby entirely or partially converting acetaldehyde contained in the reaction mass into acetaldoxime, and then separating or removing the acetaldoxime from the reaction mass;

7. The method for obtaining propylene oxide according to

the above item 6, wherein the recovery step is a step of recovering propylene oxide existing in the reaction mass which is obtained by feeding, as a liquid gas, a reaction mass obtained by reacting the both raw materials into a gas-liquid separator, and separating into a reaction mass as a liquid part and a gas as a gas part under a pressure which is the same as or lower than that obtained in the reaction;

8. The method for obtaining propylene oxide according to the above item 6 or 7, wherein the hydroxylamine compound is hydroxylamine sulfate or hydroxylamine hydrochloride;

9. The method for obtaining propylene oxide according to any one of the above items 6 to 8, wherein the separation/removal step is a step of distilling a reaction mass before removing acetaldoxime, and the distillation step includes a step of separating or removing by recovering a top liquid of a distillation column, which contains acetonitrile, from a top section of the column and also recovering a bottom liquid of the column, which contains acetaldoxime, from a bottom section of the column;

10. The method for obtaining propylene oxide according to any one of the above items 1 to 9, wherein the catalyst is titanosilicate catalyst and also the raw material (a) is hydrogen peroxide;

11. The method for obtaining propylene oxide according to any one of the above items 1 to 9, wherein the catalyst

includes both a titanosilicate catalyst and a catalyst obtained by supporting palladium on a carrier, and the raw material (a) includes hydrogen and oxygen;

12. The method for obtaining propylene oxide according to the above item 11, wherein the noble metal catalyst is palladium;

13. The method for obtaining propylene oxide according to the above item 10 or 11, wherein the titanosilicate catalyst is a Ti-MWW precursor.

Advantageous Effects of Invention

[0006]

According to the present invention, it becomes possible to provide a method for obtaining propylene oxide in which a content of acetaldehyde is reduced.

Brief Description of Drawings

[0007]

Fig. 1 is a flow chart showing an example of an embodiment, in which the processes of the production of propylene oxide are schematically illustrated. The process between (1) and (5) in the flow chart corresponds to the separation/removal step, and the process between (6) and (7) in the flow chart corresponds to the recovery step. An epoxidation reaction is performed in the process between (1) and (3) in the flow chart, and an oximation reaction is

performed in the process (5) in the flow chart.

Fig. 2 is a flow chart showing an example of an embodiment, in which the processes of the production of propylene oxide are schematically illustrated. The process between (1) and (4) and the process (6) in the flow chart corresponds to the recovery step, and the process between (5) and (7) in the flow chart corresponds to the separation/removal step. An epoxidation reaction is performed in the process between (1) and (3) in the flow chart, and an oximation reaction is performed in the process (5) in the flow chart.

Description of Embodiments

[0008]

The present invention includes both a first obtaining method of the present invention and a second obtaining method of the present invention (hereinafter sometimes referred collectively to as an obtaining method of the present invention).

The first obtaining method of the present invention is a method for obtaining propylene oxide, which includes the steps of:

mixing a hydroxylamine compound in a reaction mass which is obtained by reacting main raw materials in an acetonitrile-containing solvent in the presence of a catalyst (the reaction corresponds to the below-defined

"epoxidation reaction"), thereby entirely or partially converting acetaldehyde contained in the reaction mass into acetaldoxime (the reaction corresponds to the below-defined "oximation reaction"), and then separating or removing the acetaldoxime from the reaction mass; and

recovering the reaction mass obtained by the former step or propylene oxide existing in the reaction mass.

On the other hand, the second obtaining method of the present invention is a method for obtaining propylene oxide, which includes steps of:

recovering propylene oxide existing in a reaction mass which is obtained by reacting main raw materials in an acetonitrile-containing solvent in the presence of a catalyst (the reaction corresponds to the below-defined "epoxidation reaction"); and

mixing a hydroxylamine compound in the reaction mass obtained after recovering propylene oxide by the former step, thereby entirely or partially converting acetaldehyde contained in the reaction mass into acetaldoxime (the reaction corresponds to the below-defined "oximation reaction"), and then separating or removing the acetaldoxime from the reaction mass.

[0009]

The epoxidation reaction in the obtaining method of the present invention will be described below.

[0010]

In the obtaining method of the present invention, examples of the catalyst to be used to react main raw materials in an acetonitrile-containing solvent in the presence of a catalyst (hereinafter, the reaction is sometimes referred to as an "epoxidation reaction") include both of (1) a titanosilicate catalyst such as a Ti-MWW precursor and (2) a catalyst obtained by supporting the titanosilicate catalyst and a noble metal catalyst such as palladium on a carrier, and the like.

10 [0011]

The content of the noble metal in the noble metal catalyst is, for example, within a range from 0.01% by weight to 20% by weight, and preferably from 0.1% by weight to 5% by weight.

15 [0012]

In the case where the titanosilicate catalyst is used as the catalyst, examples of the "raw material (a)" as one of raw materials to be used in the obtaining method of the present invention include hydrogen peroxide and the like.

20 In the case where both of the titanosilicate catalyst and the catalyst obtained by supporting a noble metal catalyst such as palladium on a carrier is used as the catalyst, examples of the "raw material (a)" as one of raw materials to be used in the obtaining method of the present invention include hydrogen, oxygen and the like.

25

[0013]

When both of the titanosilicate catalyst and the catalyst obtained by supporting a noble metal catalyst such as palladium on a carrier are used as the catalyst, the use amount of the noble metal is, for example, 0.00001 part by weight or more, preferably 0.0001 part by weight or more, and more preferably 0.001 part by weight or more, based on 1 part by weight of the titanosilicate catalyst. The existing amount of the "catalyst obtained by supporting a noble metal catalyst such as palladium on a carrier" relative to the "titanosilicate catalyst" is, for example, 100 parts by weight or less, preferably 20 parts by weight or less, and more preferably 5 parts by weight or less, based on 1 part by weight of the titanosilicate catalyst.

[0014]

The titanium silicate catalyst substantially means titanosilicate including tetrahedrally coordinated Ti in which an ultraviolet-visible absorption spectrum in a wavelength range of 200 nm to 400 nm exhibits a maximum absorption peak in a wavelength range of 210 nm to 230 nm (see, for example, Chemical Communications 1026-1027, (2002) Fig. 2(d) and Fig. 2(e)). The ultraviolet-visible absorption spectrum can be measured by a diffuse reflectance method using an ultraviolet-visible spectrophotometer with an attached diffuse reflector.

[0015]

It is possible to exemplify, as preferred

titanosilicate catalysts, catalysts having pores composed of a 10- or more membered oxygen ring since inhibition of contact between reaction raw materials and an active spot in pores may be reduced and limitation of movement of substances in pores may be reduced.

Herein, "pores" mean pores composed of Si-O bonds or Ti-O bonds. Examples of pores include half-cup shaped pores called a side pocket (i.e., it is not necessary to penetrate primary particles of titanosilicate) and the like.

"10- or more membered oxygen ring" means 10 or more carbon atoms in (a) a cross section of the thinnest area in pores, or (b) a ring structure in a pore inlet. It is generally confirmed by analysis of an X-ray diffraction pattern that the titanosilicate catalyst has pores composed of a 10- or more membered oxygen ring. A known structure can be simply confirmed by comparing with an X-ray diffraction pattern thereof.

[0016]

Specific examples of such a titanosilicate catalyst include those described in the following 1 to 7 and the like.

[0017]

1. Crystalline titanosilicate having pores composed of a 10-membered oxygen ring:

TS-1 having MFI structure according to the structure code of the International Zeolite Association (IZA) (for example,

U.S. Patent No. No. 4,410,501), TS-2 having a MEL structure (for example, Journal of Catalysis 130, 440-446, (1991)), Ti-ZSM-48 having a MRE structure (for example, Zeolites 15, 164-170, (1995)), Ti-FER having a FER structure (for example, Journal of Materials Chemistry 8, 1685-1686 (1998)) and the like.

[0018]

2. Crystalline titanosilicate having pores composed of a 12-membered oxygen ring:

10 Ti-Beta having a BEA structure (for example, Journal of Catalysis 199, 41-47, (2001)), Ti-ZSM-12 having a MTW structure (for example, Zeolites 15, 236-242, (1995)), Ti-MOR having a MOR structure (for example, The Journal of Physical Chemistry B 102, 9297-9303, (1998)), Ti-ITQ-7
15 having a ISV structure (for example, Chemical Communications 761-762, (2000)), Ti-MCM-68 having a MSE structure (for example, Chemical Communications 6224-6226, (2008)), Ti-MWW having a MWW structure (for example, Chemistry Letters 774-775, (2000)) and the like.

20 [0019]

3. Crystalline titanosilicate having pores composed of 14-membered oxygen ring:

Ti-UTD-1 having a DON structure (for example, Studies in Surface Science and Catalysis 15, 519-525, (1995)) and the
25 like.

[0020]

4. Layered titanasilicate having pores composed of a 10-membered oxygen ring:

Ti-ITQ-6 (for example, Angewandte Chemie International Edition 39, 1499-1501, (2000)) and the like.

5 [0021]

5. Layered titanasilicate having pores composed of a 12-membered oxygen ring:

Ti-MWW precursor (for example, EP1731515A1), Ti-YNU-1 (for example, Angewandte Chemie International Edition 43, 236-240, (2004)), Ti-MCM-36 (for example, Catalysis Letters 113, 160-164, (2007)), Ti-MCM-56 (for example, Microporous and Mesoporous Materials 113, 435-444, (2008)) and the like

[0022]

6. Mesoporous titanasilicate:

15 Ti-MCM-41 (for example, Microporous Materials 10, 259-271, (1997)), Ti-MCM-48 (for example, Chemical Communications 145-146, (1996)), Ti-SBA-15 (for example, Chemistry of Materials 14, 1657-1664, (2002)) and the like.

[0023]

20 7. Silylated titanasilicate:

Compounds obtained by silylating titanosilicates described in the above 1 to 6, such as silylated Ti-MWW.

[0024]

Herein, "layered titanasilicate" is a generic term of
25 titanasilicate having a layered structure, for example, a layered precursor of a crystalline titanasilicate, a

titanosilicate in which the interlayer distance of the crystalline titanosilicate is increased, and the like. It is possible to confirm that the titanosilicate has a layered structure by an electron microscope or the measurement of an X-ray diffraction pattern. The "layered precursor" means a titanosilicate which forms a crystalline titanosilicate by performing a treatment such as dehydration condensation. It is possible to easily judge by a structure of the corresponding crystalline titanosilicate that the layered titanosilicate has pores composed of a 12- or more membered oxygen ring.

[0025]

The "mesoporous titanosilicate" is a generic term of a titanosilicate having regular mesopores. The regular mesopores mean a structure in which mesopores are regularly repeat-arranged. The "mesopores" mean pores each having a pore diameter of 2 nm to 10 nm.

[0026]

The "silylated titanosilicate" is a compound obtained by treating the titanosilicate described in the above 1 to 4 with a silylating agent. Examples of the silylating agent include 1,1,1,3,3,3-hexamethyldisilazane, trimethylchlorosilane and the like (for example, EP1488853A1).

[0027]

In the obtaining method of the present invention, a

titanosilicate catalyst as a catalyst used to react (i.e., epoxidation reaction) main raw materials in an acetonitrile-containing solvent in the presence of the catalyst is preferably a catalyst which is brought into contact with hydrogen peroxide in advance. The concentration of hydrogen peroxide to be brought into contact is, for example, within a range from 0.0001% by weight to 50% by weight.

[0028]

Among such a titanosilicate catalyst, a titanosilicate having pores composed of a 12- or more membered oxygen ring is preferable. Such a titanosilicate may be either a crystal or a layered titanosilicate. Examples of pores composed of a 12- or more membered oxygen ring include Ti-MWW, a Ti-MWW precursor and the like.

[0029]

The Ti-MWW precursor may be synthesized by bringing a layered compound (also referred to as an as-synthesized sample), which is directly prepared through hydrothermal synthesis of a boron compound, a titanium compound, a silicon compound and a structure directing agent, into contact with an aqueous solution of a strong acid under reflux conditions to remove the structure directing agent, and then adjusting a molar ratio (Si/N ratio) of silicon to nitrogen to 21 or more (see, for example, JP-A-2005-262164). On the other hand, Catalysis Today 117 (2006) 199-205

discloses that a Ti-MWW precursor containing 13.5 to 14.2% by weight of a structure directing agent is obtained by subjecting a compound, which is obtained by mixing Ti-MWW, piperidine and water, to a hydrothermal treatment and then washed with water. As a result of CHN elemental analysis described in the same document, a molar ratio of silicon to nitrogen (Si/N ratio) of the Ti-MWW precursor was from 5 to 20, and preferably from 8.5 to 8.6, calculated from a molar ratio of silicon to titanium (Si/Ti ratio) and a molar ratio of silicon to boron (Si/B ratio). Regarding the molar ratio of silicon to nitrogen (Si/N ratio), since the content of nitrogen is higher as compared with the molar ratio (Si/N ratio) in a conventionally known Ti-MWW precursor, the Ti-MWW precursor can be used as a preferable titanosilicate catalyst (Ti-MWW precursor). Ti-MWW can be obtained by crystallizing the Ti-MWW precursor obtained as mentioned above through firing.

[0030]

The Ti-MWW precursor having a Si/N ratio of 5 to 20 (hereinafter sometimes referred to as the present precursor) will be further described below. Herein, analysis of elements contained in the sample can be performed by the following general method. Ti (titanium), Si (silicon) and B (boron) can be measured by alkaline resolution-nitric acid dissolution-ICP spectrometry, while N (nitrogen) can be measured by an oxygen circulation

combustion TCD detection system (SUMIGRAPH Model NCH-22F (manufactured by Sumika Chemical Analysis Service, Ltd.) was used in Examples of the present description). The Ti-MWW precursor is a generic term of a precursor which is converted into Ti-MWW as a crystalline titanosilicate having a MWW (according to the structure code of the International Zeolite Association (IZA)) structure by firing, while the titanosilicate is a generic term of a titanosilicate in which a part of Si in the tectosilicate is isomorphously substituted with Ti (see descriptions of item of "Titanosilicate" of Dictionary of Catalyst ("Shokubai no Jiten" in Japanese) (Asakura Publishing Co., Ltd.) published on November 1, 2000)). Isomorphous substitution of Si with Ti can be easily confirmed, for example, by the fact that an ultraviolet-visible absorption spectrum exhibits a peak at 210 nm to 230 nm. A UV-Vis spectrum of the sample used in Examples of the present description was measured by a diffuse reflectance method using an ultraviolet-visible spectrophotometer ((V-7100), manufactured by JASCO Corporation) with an attached diffuse reflector (Praying Mantis, manufactured by HARRICK Corporation).

[0031]

The present precursor can be obtained by a method in which a titanosilicate having an X-ray diffraction pattern with the value shown below is brought into contact with a

structure directing agent capable of forming zeolite having a MWW structure.

[0032]

<X-ray diffraction pattern (lattice spacing $d/\text{\AA}$)>

5 12.4 $\pm$ 0.8, 10.8 $\pm$ 0.3, 9.0 $\pm$ 0.3, 6.0 $\pm$ 0.3, 3.9 $\pm$ 0.1, 3.4 $\pm$ 0.1

[0033]

These X-ray diffraction patterns may be measured by a general X-ray diffractometer using copper K-alpha radiation.

[0034]

10 Examples of the titanosilicate having an X-ray diffraction pattern shown below include a Ti-MWW precursor (for example, those described in JP-A-2005-262164), Ti-YNU-1 (for example, those described in Angewandte Chemie International Edition) 43, 236-240, (2004)), crystalline
15 titanosilicates Ti-MWW (for example, those described in JP-A-2003-327425) as a crystalline titanosilicate having a MWW structure according to the structure code of the International Zeolite Association (IZA), Ti-MCM-68 (for example, those described in JP-A-2008-50186) as a
20 crystalline titanosilicate having a MSE structure according to the structure code of IZA and the like.

[0035]

The present precursor may be usually synthesized by bringing a layered compound (see, for example, Chemistry
25 Letters 774-775 (2000), described as an as-synthesized sample in the same document), which is obtained by mixing a

silicon compound, a boron compound, a titanium compound, water and a structure directing agent, and then subjecting the mixture to a heat treatment, into contact with 2M nitric acid to remove the structure directing agent. The
5 above-mentioned layered compound called as the as-synthesized sample is converted into a zeolite having a MWW structure when this layered compound is fired as it is. However, the zeolite is not a titanosilicate catalyst since an ultraviolet-visible absorption spectrum does not
10 exhibits a peak at 210 nm to 230 nm.

[0036]

The present precursor can also be produced by preferably bringing a layered borosilicate, which is obtained by heating a mixture containing a structure
15 directing agent, a boron compound, a silicon compound and water, into contact with acid or the like to remove the structure directing agent, firing the product to obtain B-MWW, removing boron from the thus obtained B-MWW using an acid or the like, adding a structure directing agent, a
20 titanium compound and water to obtain a mixture, heating the mixture to obtain a layered compound, and then bringing the layered compound into contact with 6M nitric acid to remove the structure directing agent (for example, Chemical Communication 1026-1027, (2002)).

25 [0037]

Furthermore, the present precursor can also be

produced by bringing a layered borosilicate, which is obtained by heating a mixture containing a structure directing agent, a boron compound, a silicon compound and water, into contact with a titanium source and an inorganic acid to remove the structure directing agent.

[0038]

The Ti-MWW precursor, which is obtained from the layered compound obtained by various methods as mentioned above, has an Si/N ratio of 21 or more, and the Ti-MWW precursor is converted into Ti-MWW, in which an ultraviolet-visible absorption spectrum exhibits a peak at 210 nm to 230 nm, by firing at a temperature of 530°C.

[0039]

Examples of the structure directing agent (i.e., a structure directing agent capable of forming a zeolite having a MWW structure) include piperidine, hexamethyleneimine, an *N,N,N*-trimethyl-1-adamantaneammonium salt (for example, *N,N,N*-trimethyl-1-adamantaneammonium hydroxide, *N,N,N*-trimethyl-1-adamantaneammonium iodide, etc.), an octyltrimethyl ammonium salt (for example, octyltrimethylammonium hydroxide, octyltrimethylammonium bromide, etc.) (see, for example, Chemistry Letters 916-917 (2007)) and the like. Preferably, for example, piperidine, hexamethyleneimine and the like are exemplified. These compounds may be used alone, or two or more kinds may be used in the form of a mixture at any mixing ratio.

[0040]

The amount of the structure directing agent to be used to form a zeolite having a MWW structure is from 0.001 time to 100 times, and preferably from 0.1 time to 10 times, in terms of a ratio of the weight of the structure directing agent to the weight of the titanosilicate.

[0041]

Contact between the structure directing agent and the titanosilicate may be usually performed by heating under pressure in a closed container such as an autoclave, and also can be performed by a method of mixing in a flask made of glass while stirring under atmospheric pressure, or mixing without stirring. The temperature in case of contacting is, for example, from 0°C to 250°C, and preferably from 50°C to 200°C. The pressure in case of contacting is, for example, from 0 MPa to 10 MPa in terms of a gauge pressure. The present precursor obtained after contacting is usually separated by filtration. The present precursor having a Si/N ratio within a range from 5 to 20 is obtained by optionally washing with water or the like. Washing may be performed by appropriately adjusting the amount of a wash, the pH of a washing filtrate and the like while optionally monitoring.

[0042]

The present precursor thus produced can be used as a catalyst in an oxidation reaction or the like. The Si/N

ratio of the present precursor is, for example, within a range from 10 to 20, and preferably from 10 to 16. The present precursor may be silylated using a silylating agent, for example, 1,1,1,3,3,3-hexamethyldisilazane or the like.

5 [0043]

A ratio (S_{H_2O}/S_{N_2}) of a specific surface area value (S_{H_2O}) measured by a steam adsorption method to a specific surface area value (S_{N_2}) measured by a nitrogen adsorption method in the present precursor is, for example, within a
10 range from 0.7 to 1.5, and preferably from 0.8 to 1.3. The specific surface area value (S_{N_2}) measured by nitrogen adsorption may be determined by degassing a sample at 150°C, measuring, for example, through a nitrogen adsorption method using "BELSORP-mini" (manufactured by BEL Japan,
15 Inc.), followed by calculation through a BET method. The specific surface area value (S_{H_2O}) measured by steam adsorption may be determined by degassing a sample at 150°C, measuring, for example, through a steam adsorption method at an adsorption temperature of 298 K using "BELSORP-aqua3"
20 (manufactured by BEL Japan, Inc.), followed by calculation through a BET method.

[0044]

With respect to the "raw material (a)" as one of raw materials to be used to react (i.e., epoxidation reaction)
25 main raw materials in an acetonitrile-containing solvent in the presence of a catalyst in the obtaining method of the

present invention, "hydrogen peroxide" used as the "raw material (a)" may be a commercially available product (i.e., hydrogen peroxide solution) and may be generated from "hydrogen and oxygen" used as the "raw material (a)" by a noble metal catalyst such as palladium.

The concentration of hydrogen peroxide varies depending on the kind, reaction conditions and the like and, for example, the concentration of hydrogen peroxide in the hydrogen peroxide solution is within a range from 0.0001% by weight to 100% by weight, and more preferably from 0.001% by weight to 5% by weight.

The amount of the hydrogen peroxide varies depending on the kind, reaction conditions and the like and, for example, a ratio (molar ratio) of the amount of hydrogen peroxide to the amount of propylene as the raw material (b) existing in the reaction system is within a range from 1,000: 1 to 1: 1,000.

[0045]

In the obtaining method of the present invention, the "hydrogen peroxide" among the "raw material (a)" as one of raw materials to be used to react (i.e., epoxidation reaction) main raw materials in an acetonitrile-containing solvent in the presence of a catalyst, may be fed in a state of being dissolved in the below-mentioned solvents such as water and acetonitrile. By the way, in case of using hydrogen peroxide in a state of being dissolved in

the solvent other than acetonitrile, a reaction mass containing the solvent can be obtained.

[0046]

Examples of the solvent other than acetonitrile used to dissolve the hydrogen peroxide include an alcohol solvent, a ketone solvent, a nitrile solvent, an ether solvent, an aliphatic hydrocarbon, an aromatic hydrocarbon, a halogenated hydrocarbon, an ester solvent, a mixture thereof and the like.

[0047]

Examples of the alcohol solvent include aliphatic alcohols having 1 to 8 carbon atoms, such as methanol, ethanol, isopropanol and t-butanol; glycols having 2 to 8 carbon atoms, such as ethylene glycol and propylene glycol; and the like. Monohydric alcohols having 1 to 4 carbon atoms are preferable, and t-butanol is more preferable.

Examples of the aliphatic hydrocarbon include aliphatic hydrocarbons having 5 to 10 carbon atoms, such as hexane and heptane, and the like.

Examples of the aromatic hydrocarbon include aromatic hydrocarbon having 6 to 15 carbon atoms, such as benzene, toluene and xylene, and the like.

Examples of the nitrile solvent include alkylnitriles having 2 to 4 carbon atoms, such as propionitrile, isobutyronitrile and butyronitrile; benzonitriles; and the like.

[0048]

Examples of the acetonitrile used to dissolve hydrogen peroxide include purified acetonitrile, crude acetonitrile by-produced in the production process of acrylonitrile and the like. Examples of impurities other than acetonitrile contained in the crude acetonitrile include water, acetone, acrylonitrile, oxazole, allyl alcohol, propionitrile, hydrocyanic acid, ammonia, copper, iron and the like. The content of copper and iron is preferably a trace amount of 1% by weight or less.

Purity of the acetonitrile is, for example, 95% by weight or more, preferably 99% by weight or more, and more preferably 99.9% by weight or more.

[0049]

Examples of the noble metal catalyst such as palladium used to generate "hydrogen peroxide" from "oxygen and hydrogen" in the present invention include catalysts containing noble metals such as palladium, platinum, ruthenium, rhodium, iridium, osmium and gold; or alloy or mixtures of these noble metals. Examples of preferable noble metal include palladium, platinum, gold and the like. Examples of more preferable noble metal include palladium and the like.

[0050]

The above-mentioned palladium or the below-mentioned palladium compound may be used, for example, in the form of

colloids (see, for example, JP-A-2002-294301, Example 1).

[0051]

The content of the noble metal in the noble metal catalyst is, for example, within a range from 0.01% by weight to 20% by weight, and preferably from 0.1% by weight to 5% by weight.

[0052]

When the noble metal catalyst is a noble metal compound and the noble metal is palladium, it is also possible to use a mixture of the noble metal compound, and noble metals other than palladium, such as platinum, rhodium, iridium, osmium and gold added thereto. Examples of preferable noble metal other than palladium include platinum, gold and the like.

[0053]

Examples of the palladium compound include tetravalent palladium compounds such as sodium hexachloropalladate (IV) tetrahydrate and potassium hexachloropalladate (IV); divalent palladium compounds such as palladium (II) chloride, palladium (II) bromide, palladium (II) acetate, palladium (II) acetylacetonate, dichlorobis(benzonitrile) palladium (II), dichlorobis(acetonitrile) palladium (II), dichloro(bis(diphenylphosphino)ethane) palladium (II), dichlorobis(triphenylphosphine) palladium (II), dichlorotetraammine palladium (II) dibromotetraammine palladium (II), dichloro(cycloocta-1,5-diene) palladium

(II), and palladium (II) trifluoroacetate; and the like.

[0054]

The noble metal catalyst such as a palladium used to generate "hydrogen peroxide" from "oxygen and hydrogen" in the present invention may be a noble metal catalyst in a state of being supported on a carrier. Herein, examples of the "carrier" include carbon; oxides such as silica, alumina, titania, zirconia and niobia; hydrates such as niobic acid, zirconic acid, tungstic acid and titanic acid; mixtures thereof; noble metal catalysts such as a palladium; and the like.

[0055]

Examples of the method for preparing a noble metal catalyst in a state of being supported on a carrier among noble metal catalysts such as a palladium used to generate "hydrogen peroxide" from "oxygen and hydrogen" in the present invention include a conventional method such as an impregnation method. The noble metal catalyst obtained by a conventional method such as an impregnation method may be subjected to a reduction treatment using a reducing gas. Examples of the method of the reduction treatment include a method in which a reduction treatment is performed by injecting a reducing gas into a packed tube filled with a solid noble metal catalyst. Herein, examples of the "reducing gas" include hydrogen, carbon monoxide, methane, ethane, propane, butane, ethylene, propylene, butene,

butadiene, or a mixed gas of two or more kinds selected from these gases. Among them, hydrogen is preferable. Examples of the reducing gas include nitrogen, helium, argon, steam, or a mixed gas thereof.

5 [0056]

When "hydrogen peroxide" is generated from "oxygen and hydrogen" with a noble metal catalyst such as a palladium in the present invention, a partial pressure ratio of oxygen to hydrogen (oxygen:hydrogen) in a mixed gas of oxygen and hydrogen to be fed in a reactor is, for example, within a range from 1:50 to 50:1, and preferably from 1:10 to 10:1. It is preferred that the partial pressure of oxygen is more than 1:50 in terms of oxygen:hydrogen since the formation rate of propylene oxide may increase. It is preferred that the partial pressure of oxygen is less than 50:1 in terms of oxygen:hydrogen since the formation of by-products in which a carbon-carbon double bond of propylene is reduced with a hydrogen atom is reduced, and thus selectivity to propylene oxide may be improved.

20 [0057]

It is preferred to handle a mixed gas of oxygen and hydrogen in the presence of a diluent gas. Herein, examples of the "diluent gas" include nitrogen, argon, carbon dioxide, methane, ethane, propane and the like. Among them, nitrogen and propane are preferable, and nitrogen is more preferable.

[0058]

In case of handling a mixture of oxygen, hydrogen, propylene and a diluent gas, a mixing ratio thereof will be described by way of the case where the diluent gas is a nitrogen gas, as an example. It is preferred the case where the total concentration of hydrogen and propylene is 4.9% by volume or less, the concentration of oxygen is 9% by volume or less and the balance is a nitrogen gas, or the case where the total concentration of hydrogen and propylene is 50% by volume or more, the concentration of oxygen is 50% by volume or less and the balance is a nitrogen gas.

[0059]

An oxygen gas, and air containing oxygen may be used as oxygen. Examples of the oxygen gas include an oxygen gas produced by an inexpensive pressure swing method, a high purity oxygen gas produced by cryogenic separation and the like.

The feed amount of oxygen is, for example, within a range from 0.005 to 10 mol, and preferably from 0.05 to 5 mol, based on 1 mol of propylene to be fed.

[0060]

Examples of hydrogen include those obtained by steam-reforming hydrogen and the like. Purity of hydrogen is 80% by volume or more, and preferably 90% by volume or more. The feed amount of hydrogen is, for example, within a range

from 0.05 to 10 mol, and preferably from 0.05 to 5 mol, based on 1 mol of propylene to be fed.

[0061]

When "hydrogen peroxide" is generated from "oxygen and hydrogen" with a noble metal catalyst such as a palladium in the present invention, it is preferred to allow a quinoid compound to exist in the reaction system since it may further increase selectivity to an oxirane compound.

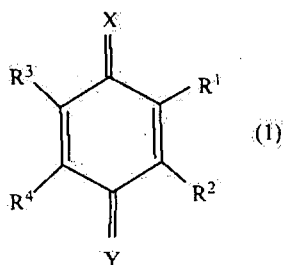
In the case of using the quinoid compound, a quinoid compound-containing solution is usually obtained from a discharging tube of bottom liquid of a first distillation column connected to the bottom section of the below-mentioned first distillation column. In some cases, a quinoid compound crystal may be obtained.

The obtained quinoid compound crystal is usually separated by filtration. Examples of the filtration system include a pressurization system, a centre system and the like. In order to remove impurities after filtration, the quinoid compound crystal may be washed with a mixed solution of water and a hydrophilic organic solvent. The filtration temperature may be, for example, the same temperature as the crystallization temperature. The thus obtained quinoid compound (i.e., a recovered quinoid compound) may be, for example, recycled to an epoxidation reaction by drying to form a dry cake, or recycled in the form of a wet cake, or recycled after dissolving in a mixed

solution of acetonitrile and water, or recycled after forming a slurry using a mixed solution of acetonitrile and water. The quinoid compound is preferably recycled, for example, after dissolving in a mixed solution of acetonitrile and water.

[0062]

Examples of the quinoid compound include a compound represented by the formula (1):



wherein R^1 , R^2 , R^3 and R^4 each independently represents hydrogen atom, or R^1 and R^2 , or R^3 and R^4 may be taken together with a carbon atom to which R^1 , R^2 , R^3 and R^4 are attached to form a benzene ring which may have a substituent, or a naphthalene ring which may have a substituent. X and Y each independently represents an oxygen atom or a NH group.

[0063]

Examples of the compound represented by the formula (1) include:

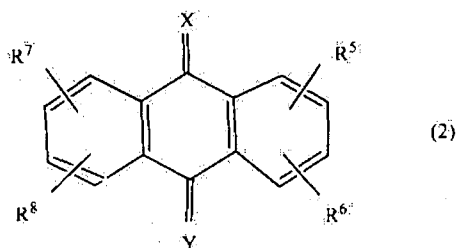
- 1) a quinone compound (1A) in which R^1 , R^2 , R^3 and R^4 in the formula (1) are hydrogen atoms, and both X and Y are oxygen atoms,
- 2) a quinoneimine compound (1B) in which R^1 , R^2 , R^3 and R^4

in the formula (1) are hydrogen atoms, X is an oxygen atom and Y is an NH group, and

3) a quinonediimine compound (1C) in which R^1 , R^2 , R^3 and R^4 in the formula (1) are hydrogen atoms, and X and Y are
5 NH groups.

[0064]

Other Examples of the compound represented by the formula (1) include an anthraquinone compound represented by the formula (2):



10 wherein X and Y are as defined in the formula (1), R^5 , R^6 , R^7 and R^8 each independently represents a hydrogen atom, a hydroxyl group or an alkyl group (for example, alkyl groups having 1 to 5 carbon atoms, such as a methyl group, an
15 ethyl group, a propyl group, a butyl group and a pentyl group)).

[0065]

Examples of X and Y in the compound represented by the formula (1) preferably include an oxygen atom.

20 Examples of the compound represented by the formula (1) include quinone compounds such as benzoquinone and naphthoquinone; anthraquinones; 2-alkylanthraquinone compounds such as 2-ethylanthraquinone, 2-t-

butylanthraquinone, 2-amylanthraquinone, 2-methylanthraquinone, 2-butylanthraquinone, 2-t-amylanthraquinone, 2-isopropylanthraquinone, 2-s-butylanthraquinone and 2-s-amylanthraquinone;

5 polyalkylanthraquinone compounds such as 1,3-diethylanthraquinone, 2,3-dimethylanthraquinone, 1,4-dimethylanthraquinone and 2,7-dimethylanthraquinone; polyhydroxyanthraquinone compounds such as 2,6-dihydroxyanthraquinone; *p*-quinoid compounds such as
10 naphthoquinone and 1,4-phenanthraquinone; *o*-quinoid compounds such as 1,2-phenanthraquinone, 3,4-phenanthraquinone and 9,10-phenanthraquinone; and the like. Preferably, examples thereof include anthraquinone, a 2-alkylanthraquinone compound (X and Y in the formula (2)
15 represent an oxygen atom, R⁵ represents an alkyl group, R⁶ represents hydrogen, and R⁷ and R⁸ represent a hydrogen atom) and the like.

[0066]

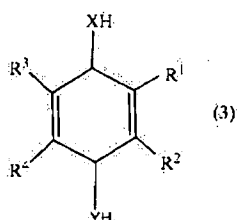
In the present invention, the use amount of such a
20 quinoid compound is within a range from 0.001 mmol to 500 mmol, and preferably from 0.01 mmol to 50 mmol, based on 1 kg of the solvent.

[0067]

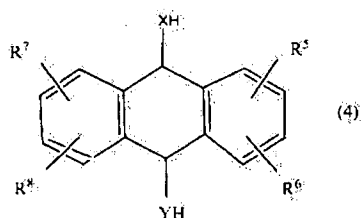
The quinoid compound can also be prepared by oxidizing
25 a dihydro form of the quinoid compound using oxygen in the reaction system. For example, oxidation with oxygen may be

performed in the reaction system by adding a quinoid compound such as 9,10-anthracenediol or a compound obtained by hydrogenating hydroquinone or the like in a liquid phase to generate a quinoid compound, and the obtained quinoid compound may be used.

Examples of the "dihydro form of the quinoid compound" include a compound represented by the formula (3):



wherein R^1 , R^2 , R^3 , R^4 , X and Y have the same meanings as defined above, as a dihydro form of a compound represented by the formula (1), and a compound represented by the formula (4):



wherein X, Y, R^5 , R^6 , R^7 and R^8 have the same meanings as defined above, as a dihydro form of a compound represented by the formula (2).

Among the compound represented by the formula (3) and the compound represented by the formula (4), preferred compound is a dihydro form corresponding to the above-mentioned preferred quinoid compound. X and Y in the

compound represented by the formula (3) and the compound represented by the formula (4) are preferably, for example, oxygen atoms.

[0068]

5 In the obtaining method of the present invention, the "raw material (b)" as one of raw materials to be used to react (i.e., epoxidation reaction) main raw materials in an acetonitrile-containing solvent in the presence of a catalyst, is propylene.

10 Examples of the propylene include those produced by pyrolysis, heavy oil catalytic cracking or methanol catalytic reforming.

 The propylene may be purified propylene, or crude propylene obtained without subjecting to the purification
15 step. Preferred propylene is, for example, propylene having a purity of 90% by volume or more, and preferably 95% by volume or more.

 Examples of impurities contained in propylene include propane, cyclopropane, methylacetylene, propadiene,
20 butadiene, butanes, butenes, ethylene, ethane, methane, hydrogen and the like.

 Examples of the form of the propylene include gas, liquid and the like. Herein, examples of "liquid" include (i) liquid of propylene alone, (ii) a mixed solution in
25 which propylene is, for example, dissolved in an organic solvent or a mixed solvent of an organic solvent and water.

Examples of "gas" include (i) gas of propylene alone, (ii) a mixed gas of gaseous propylene and the other gas component such as a nitrogen gas or a hydrogen gas.

[0069]

5 The amount of the propylene varies depending on the kind, reaction conditions and the like, and is 0.01 part by weight or more, and more preferably 0.1 part by weight or more, based on 100 parts by weight of the amount of a mixture of an acetonitrile-containing solvent existing in
10 the reaction system, a catalyst and main raw materials.

[0070]

 The amount of a titanosilicate catalyst among the catalyst varies depending on the kind, reaction conditions and the like, and is, for example, within a range from 0.01
15 part by weight to 20 parts by weight, preferably from 0.1 part by weight to 10 parts by weight, and more preferably from 0.5 part by weight to 8 parts by weight, based on 100 parts by weight of a mixture of an acetonitrile-containing solvent existing in the reaction system, a catalyst and
20 main raw materials.

[0071]

 The "acetonitrile-containing solvent" means a solvent containing acetonitrile, and the acetonitrile-containing solvent may contain solvents other than acetonitrile.

25 Examples of solvents other than acetonitrile include organic solvents other than acetonitrile, water and the

like. The weight proportion of acetonitrile in the acetonitrile-containing solvent is, for example, preferably within a range of 50% or more, and more preferably from 60% to 100%.

5 [0072]

In the obtaining method of the present invention, the reaction temperature at which main raw materials are reacted (i.e., epoxidation reaction) in an acetonitrile-containing solvent in the presence of a catalyst is, for example, within a range from 0°C to 200°C, and preferably from 40°C to 150°C. The reaction pressure (gauge pressure) is, for example, 0.1 MPa or more, preferably 1 MPa or more, more preferably 10 MPa or more, and still more preferably 20 MPa or more, under pressure.

15 [0073]

In the obtaining method of the present invention, in order to react (i.e., epoxidation reaction) main raw material in an acetonitrile-containing solvent in the presence of a catalyst, an ammonium salt, an alkyl ammonium salt and an alkylaryl ammonium salt may be allowed to exist in the reaction system.

It is possible to allow a buffer agent to exist in the reaction system since it may prevent reduction of catalyst activity or may further increase catalyst activity, or may increase utilization efficiency of oxygen and hydrogen. Herein, the "buffer agent" means a compound which exerts a

buffer action on the concentration of hydrogen ions of the solution, such as a salt.

The amount of the buffer agent is, for example, a value of solubility or less of the buffer agent in a mixture of an acetonitrile-containing solvent, a catalyst and main raw materials, which exists in the reaction system, and is preferably within a range from 0.001 mmol to 100 mmol, based on 1 kg of the mixture.

[0074]

Examples of the buffer agent include buffer agents composed of (1) an anion selected from the group consisting of a sulfate ion, a hydrogen sulfate ion, a carbonate ion, a hydrogen carbonate ion, a phosphate ion, a hydrogen phosphate ion, a dihydrogen phosphate ion, a hydrogen pyrophosphate ion, a pyrophosphate ion, a halogen ion, a nitrate ion, a hydroxide ion and C₁-C₁₀ carboxylate ion, and (2) a cation selected from the group consisting of ammonium, C₁-C₂₀ alkylammonium, C₇-C₂₀ alkylarylammonium, alkali metals and alkali earth metals

Herein, specific examples of the "C₁-C₁₀ carboxylate ion" include a formate ion, an acetate ion, a propionate ion, a butyrate ion, a valerate ion, a caproate ion, a caprylate ion, a capric acid ion and a benzoic acid ion. Specific examples of the "alkylammonium" include tetramethylammonium, tetraethylammonium, tetra-n-propylammonium, tetra-n-butylammonium and

cetyltrimethylammonium. Specific examples of the "cation selected from the group consisting of alkali metal and alkaline-earth metal" include a lithium cation, a sodium cation, a potassium cation, a rubidium cation, a cesium cation, a magnesium cation, a calcium cation, a strontium cation, a barium cation and the like.

[0075]

Specific examples of preferred buffer agent include ammonium salts of inorganic acids, such as ammonium sulfate, ammonium hydrogen sulfate, ammonium carbonate, ammonium hydrogen carbonate, diammonium hydrogen phosphate, ammonium dihydrogen phosphate, ammonium phosphate, ammonium hydrogen pyrophosphate, ammonium pyrophosphate, ammonium chloride and ammonium nitrate; and ammonium salts of C₁ to C₁₀ carboxylic acids, such as ammonium benzoate and ammonium acetate. Examples of preferred ammonium salt include ammonium benzoate, ammonium dihydrogen phosphate, diammonium hydrogen phosphate and the like.

[0076]

In the obtaining method of the present invention, when main raw materials are reacted (i.e., epoxidation reaction) in an acetonitrile-containing solvent in the presence of a catalyst, it is preferred that the reaction is continuously performed. For example, main raw materials are continuously fed in an epoxidation reaction tank containing an acetonitrile-containing solvent and a catalyst, and then

an epoxidation reaction is allowed to proceed in the epoxidation reaction tank, and thus leading to the subsequent step.

Herein, hydrogen and oxygen, and propylene to be continuously fed in the epoxidation reaction tank may be continuously fed as a mixed gas which is optionally mixed with a diluent gas. Propylene may be fed as a liquid.

[0077]

The epoxidation reaction tank is preferably equipped with mixing means such as a stirring blade. When equipped with the mixing means, hydrogen peroxide may be efficiently mixed with the catalyst.

Examples of one of embodiments of a specific epoxidation reaction tank include an epoxidation reaction tank denoted by (3) in Fig. 1 (hereinafter sometimes referred to as an epoxidation reaction tank (3)).

The epoxidation reaction tank (3) includes a paddle blade therein, and also includes a feeding tube of raw materials of an epoxidation reaction, denoted by the reference numeral (9) in Fig. 1, for continuously receiving a mixed gas containing oxygen, hydrogen and olefin to the epoxidation reaction tank (3) (hereinafter sometimes referred to as a feeding tube of raw materials of an epoxidation reaction (9)), and an epoxidation reaction mass discharging/feeding tube, denoted by the reference numeral (12) in Fig. 1, for continuously feeding a reaction mass to

the below-mentioned gas-liquid separation tank from the
epoxidation reaction tank (3) (hereinafter sometimes
referred to as an epoxidation reaction mass
discharging/feeding tube (12)) connected thereto. The
5 reaction mass is continuously fed to the epoxidation
reaction mass discharging/feeding tube (12) from the
epoxidation reaction tank (3).

[0078]

10 A plurality of the epoxidation reaction tanks may
exist.

It is possible to exemplify, as one of embodiments of
a specific epoxidation reaction tank, for example,
epoxidation reaction tanks denoted by the reference
numerals (1) to (3) in Fig. 1 (hereinafter, the respective
15 epoxidation reaction tanks are sometimes referred to as an
epoxidation reaction tank (1), an epoxidation reaction tank
(2) and an epoxidation reaction tank (3)).

The epoxidation reaction tank (1) includes a paddle
blade therein, and also includes a feeding tube of raw
20 materials of an epoxidation reaction (9) for continuously
receiving a mixed gas containing oxygen, hydrogen and
olefin to the epoxidation reaction tank (1), and an
epoxidation reaction mass discharging/feeding tube, denoted
by the reference numeral (10) in Fig. 1, for continuously
25 feeding a reaction mass to the epoxidation reaction tank
(2) from the epoxidation reaction tank (1) (hereinafter

sometimes referred to as an epoxidation reaction mass discharging/feeding tube (10)) connected thereto. The epoxidation reaction is performed in the epoxidation reaction tank (1) and the obtained reaction mass is

5 continuously fed to the epoxidation reaction tank (2) through the epoxidation reaction mass discharging/feeding tube (10) connected to the epoxidation reaction tank (2). The epoxidation reaction tank (2) includes a paddle blade therein, and also include a feeding tube of raw materials

10 of an epoxidation reaction (9) for continuously receiving a mixed gas containing oxygen, hydrogen and olefin to the epoxidation reaction tank (2), and an epoxidation reaction mass discharging/feeding tube, denoted by the reference numeral (11) in Fig. 1, for continuously feeding a reaction

15 mass to the epoxidation reaction tank (3) from the epoxidation reaction tank (2) (hereinafter sometimes referred to as epoxidation reaction mass discharging/feeding tube (11)) connected thereto. The epoxidation reaction is performed in the epoxidation

20 reaction tank (2) and the obtained reaction mass is continuously fed to the epoxidation reaction tank (3) through the epoxidation reaction mass discharging/feeding tube (11) connected to the epoxidation reaction tank (3).

[0079]

25 In case of extracting the reaction mass from the epoxidation reaction tank, the catalyst preferably remains

in the epoxidation reaction tank. Examples of the extraction method include (i) a method in which only a supernatant of the reaction mass is extracted so that the catalyst is not introduced from the epoxidation reaction tank, (ii) a method in which the catalyst is separated and removed by providing a filter in a passage of an epoxidation reaction mass discharging/feeding tube for continuously extracting a reaction mass from the epoxidation reaction tank and the like. In the case of using a plurality of epoxidation reaction tanks, when the reaction mass is fed to the second epoxidation reaction tank from the first epoxidation reaction tank, the catalyst may be removed from the reaction mass and the reaction mass may be fed to epoxidation reaction tank of the subsequent step, in the same manner as described above.

[0080]

Examples of the epoxidation reaction tank include a flow fixed bed reactor, a flow slurry complete mixing device and the like.

In the case of using the flow slurry complete mixing device, it is possible to further feed again the catalyst, obtained by filtering the reaction mass through a filter provided inside or outside the device, into the device. Examples thereof include (i) a method in which a part of catalyst existing in the device is extracted continuously or intermittently and the extracted catalyst is subjected

to a catalyst regeneration treatment, and then the catalyst subjected to a regeneration treatment is fed again into the device, (ii) a method in which a part of catalyst existing in the device is extracted continuously or intermittently and a new catalyst is additionally fed into the device in the amount corresponding to the discharged catalyst and the like.

In the case of using the flow fixed bed reactor, for example, the epoxidation reaction tank containing a catalyst with reduced productivity of propylene oxide is subjected to a catalyst regeneration treatment so as to regenerate the catalyst. It is also possible to perform the treatment while alternately repeating the epoxidation reaction and regeneration of the catalyst. Examples of preferred catalyst to be used include those molded using a mold release agent.

[0081]

In the second obtaining method of the present invention, propylene oxide can be recovered from a reaction mass obtained through an epoxidation reaction by performing a separation operation such as distillation.

In a specific embodiment, for example, an epoxidation reaction mass discharging/feeding tube (12) for continuously feeding is connected to the below-mentioned gas-liquid separation tank (4) from the epoxidation reaction tanks denoted by the reference numerals (1) to (3)

in Fig. 2, and a reaction mass is continuously fed to the epoxidation reaction mass discharging/feeding tube (12) from the epoxidation reaction tank (3). Then, the reaction mass is fed to a gas-liquid separation tank continuously (4) as a liquid gas, and then propylene oxide existing in the reaction mass, obtained by separating into a reaction mass as a liquid part and a gas as a gas part under a pressure which is the same as or lower than that used in the epoxidation reaction, is recovered.

10 [0082]

The reaction mass as a liquid part includes, in addition to acetonitrile, propylene oxide and water, by-products such as amides, oxazolines and aldehydes by-produced in the epoxidation reaction.

15 Specific examples of amides derived from acetonitrile include acetamide, N-(2-hydroxy-propan-1-yl)acetamide, N-(1-hydroxypropan-2-yl)acetamide) and the like.

Specific examples of oxazolines include 2,4-dimethyloxazoline, 2,5-dimethyloxazoline and the like.

20 Specific examples of aldehydes include formaldehyde, acetaldehyde, propionaldehyde and the like.

Specific examples of other by-products include formic acid, acetic acid, propionic acid, hydroxyacetone, acetone and the like.

25 [0083]

For example, in a gas-liquid separation tank denoted

by the reference numeral (4) in Fig. 1 as one of
embodiments of the specific gas-liquid separator
(hereinafter sometimes referred to as gas-liquid separation
tank (4)), an epoxidation reaction mass discharging/feeding
5 tube (12) for continuously receiving a reaction mass from
the epoxidation reaction tank (3), an epoxidation reaction
mass discharging/feeding tube, denoted by the reference
numeral (13) in Fig. 1, for continuously feeding a reaction
mass as a liquid part, from which a gas part (i.e., gas
10 component) is separated, to an oximation reaction tank (5)
(hereinafter sometimes referred to as epoxidation reaction
mass discharging/feeding tube (13)), and a reaction mass
discharging tube after gas separation, denoted by the
reference numeral (14) in Fig. 1, for discharging a gas
15 from which a liquid part (i.e., gas component) is separated
(hereinafter sometimes referred to as a reaction mass
discharging tube (14) after gas separation) are connected.
Then, reaction mass as a liquid part, from which a gas part
(i.e., gas component) is separated, is continuously fed to
20 the oximation reaction tank (5).

For example, in the gas-liquid separation tank denoted
by the reference numeral (4) in Fig. 2 (i.e., gas-liquid
separation tank (4)), an epoxidation reaction mass
discharging/feeding tube (12) for continuously receiving a
25 reaction mass from the epoxidation reaction tank (3), an
epoxidation reaction mass discharging/feeding tube (13) for

continuously feeding a reaction mass as a liquid part, from which a gas part (i.e., gas component) is separated, to the first distillation column (crude propylene oxide separation column) (6), and a reaction mass discharging tube (14)

5 after gas separation, for discharging a gas part (i.e., gas component) from which a liquid part is separated, are connected. Then, a reaction mass as a liquid part, from which a gas part (i.e., gas component) is separated, is continuously fed to the first distillation column (crude propylene oxide separation column) (6).

[0084]

In the first distillation column, the theoretical plate number is within a range from 1 to 200. Regarding distillation conditions, for example, the temperature is within a range from 0°C to 300°C, the pressure is within a range from 0.005 MPa to 10 MPa, and the reflux ratio is within a range from 0.001 to 10.

[0085]

Then, by feeding the obtained reaction mass into the first distillation column (crude propylene oxide separation column) (6), a crude propylene oxide is obtained as a top liquid of the column, which contains propylene oxide, from a discharging tube of top liquid of a first distillation column (hereinafter sometimes referred to as a discharging tube of a top liquid of a first distillation column (18)), denoted by the reference numeral (18) in Fig. 2, connected

to the top section of the column. The obtained crude propylene oxide may be further purified by a known method or a method analogous thereto.

On the other hand, a solution containing acetonitrile, water, amides, oxazolines, and aldehydes is obtained from a discharging tube of bottom liquid of a first distillation column (hereinafter sometimes referred to as discharging tube of bottom liquid of a first distillation column (17)), denoted by the reference numeral (17) in Fig. 2, connected to the bottom section of the column. In the case of using a quinoid compound in the epoxidation reaction, the bottom liquid of the column is obtained as a quinoid compound-containing solution.

[0086]

In a specific embodiment after the epoxidation reaction, as shown in Fig. 1 and Fig. 2, the reaction mass from the epoxidation reaction tank (3) is continuously separated into a gas part (i.e., gas component) composed mainly of hydrogen/oxygen/nitrogen, a recovered propylene, a crude propylene oxide, a recovered solvent and a recovered quinone compound through the gas-liquid separation tank (4), the first distillation column (crude propylene oxide separation column) (6) (hereinafter sometimes referred to as a first distillation column), and the second distillation column (acetonitrile solvent separation column) (7) (hereinafter sometimes referred to

as a second distillation column). If necessary, a propane separation column, a propylene oxide purification column, and a solvent purification column may be added.

It is preferred that the recovered propylene,
5 recovered solvent and recovered quinone compound are recycled after subjecting to the epoxidation reaction again. When the recovered propylene contains, for example, impurities such as propane, cyclopropane, methylacetylene, propadiene, butadiene, butanes, butenes, ethylene, ethane,
10 methane and hydrogen, it may be optionally recycled after separation and purification.

[0087]

In the obtaining method of the present invention, regarding the hydroxylamine compound used to the reaction
15 in which acetaldehyde contained in the reaction mass is entirely or partially converted into acetaldoxime by mixing in the obtained reaction mass (hereinafter, the reaction is sometimes referred to as an "oximation reaction"), an amino group and/or a hydroxyl group may be substituted or not.

20 Specific examples thereof include hydroxylamine (NH_2OH), N-isopropylhydroxylamine, N,N-diethylhydroxylamine, N,O-dimethylhydroxylamine, O-benzylhydroxylamine, O-methylhydroxylamine, N-methylhydroxylamine, N,O-dimethylhydroxylamine, O-ethylhydroxylamine, N-ethylhydroxylamine, O,N-diethylhydroxylamine, N-phenylhydroxylamine, O-pentylhydroxylamine, O-(2-

25

methylpropyl)hydroxylamine, O-(3-methylbutyl)hydroxylamine, O-hexylhydroxylamine, O-decylhydroxylamine and O-benzylhydroxylamine. Specifically, hydroxylamine (NH_2OH) is preferably exemplified.

5 [0088]

From a viewpoint of stability, the hydroxylamine compound may be handled as a salt. Specifically, hydroxylamine sulfate or hydroxylamine hydrochloride can be preferably exemplified.

10 [0089]

The use amount of the hydroxylamine compound is, for example, within a range from 0.1 mol to 100 mol, and more preferably from 1 mol to 10 mol, based on 1 mol of acetaldehyde.

15 [0090]

In the obtaining method of the present invention, the reaction temperature used for the reaction in which acetaldehyde contained in the reaction mass is entirely or partially converted into acetaldoxime by mixing in the
20 obtained reaction mass (i.e., oximation reaction) is, for example, within a range from 0°C to 200°C, and preferably from 20°C to 150°C. The reaction pressure (gauge pressure) may be the same pressure as that used in the epoxidation reaction, or reduced after the epoxidation reaction and may
25 be normal pressure or reduced pressure. Preferably, the reaction may be performed under the same pressure as in the

prestep of the oxime reaction.

Furthermore, in the obtaining method of the present invention, the time (specifically, retention time of a reaction mass in a reaction tank for oxime reaction) used for the reaction in which acetaldehyde contained in the reaction mass is entirely or partially converted into acetaldoxime by mixing in the obtained reaction mass (i.e., oximation reaction) is, for example, 0.01 hour or more, and preferably within a range from 0.1 hour to 10 hours.

10 [0091]

The obtaining method of the present invention further includes, in addition to the epoxidation reaction, an oximation reaction in which a hydroxylamine compound is mixed in the reaction mass obtained by the reaction and then acetaldehyde contained in the reaction mass as by-products is entirely or partially converted into acetaldoxime. Herein, the oximation reaction may be carried out in any process between a gas-liquid separation tank (4) after the epoxidation reaction and the second distillation column (acetonitrile solvent separation column) (7). In the first obtaining method of the present invention, the oximation reaction is carried out as the process existing between the gas-liquid separation tank (4) after the epoxidation reaction and the first distillation column (crude propylene oxide separation column) (6) (see, for example, Fig. 1). In second obtaining method of the

present invention, the oximation reaction is carried out as the process existing between the first distillation column (crude propylene oxide separation column) (6) and the second distillation column (acetonitrile solvent separation column) (7) (see, for example, Fig. 2). As a matter of course, the oximation reaction may be carried out plural times by using these processes in combination.

[0092]

The oximation reaction in the first obtaining method of the present invention will be described in more detail below.

As mentioned above, the first obtaining method of the present invention is composed of the separation/removal step and the recovery step. The separation/removal step includes both of the process based on the epoxidation reaction and the process based on the oximation reaction.

It is possible to exemplify, as one of embodiments of the separation/removal step, the step of mixing a hydroxylamine compound in the reaction mass, which is obtained by feeding, as a liquid gas, a reaction mass obtained by reacting the main raw materials into a gas-liquid separator, and separating into a reaction mass as a liquid part and a gas as a gas part under a pressure which is the same as or lower than that obtained in the epoxidation reaction, thereby entirely or partially converting acetaldehyde contained in the reaction mass into

acetaldoxime, and then separating or removing the acetaldoxime from the reaction mass.

It is possible to exemplify, as another embodiment, an embodiment in which the separation/removal step and the recovery step are allowed to proceed simultaneously.

It is possible to preferably exemplify, as another embodiment, an embodiment in which the separation/removal step is the step of distilling a reaction mass before removing acetaldoxime, and the distillation step includes the step of separating or removing by recovering a top liquid of the column, which contains propylene oxide, from a top section of a distillation column and also recovering a bottom liquid of the column, which contains acetaldoxime and acetonitrile, from a bottom section of a distillation column.

[0093]

For example, an oximation reaction tank denoted by the reference numeral (5) in Fig. 1 (hereinafter sometimes referred to as an oximation reaction tank (5)) as one of embodiments of the specific apparatus for oximation reaction includes a paddle blade therein, and also includes an epoxidation reaction mass discharging/feeding tube (13) for continuously receiving a reaction mass from a gas-liquid separation tank (4), a hydroxylamine compound-containing solution feeding tube, denoted by the reference numeral (15) in Fig. 1, for continuously receiving a

hydroxylamine compound-containing solution (hereinafter sometimes referred to as a hydroxylamine compound-containing solution feeding tube (15)), and a reaction mass discharging/feeding tube to first distillation column after oximation reaction denoted by the reference numeral (16) in Fig. 1 (hereinafter sometimes referred to as a reaction mass discharging/feeding tube to a first distillation column after an oximation reaction (16)) connected thereto. Then, a reaction mass containing propylene oxide in which the content of acetaldehyde is reduced is obtained from the reaction mass discharging/feeding tube to a first distillation column after an oximation reaction (16). While acetaldehyde by-produced by the epoxidation reaction is modified in the oximation reaction, propylene oxide is scarcely modified/decomposed.

[0094]

In the first distillation column denoted by the reference numeral (6) in Fig. 1 (hereinafter sometimes referred to as a first distillation column (6)) as one of embodiments of the specific first distillation column, by feeding a reaction mass containing propylene oxide in which the content of acetaldehyde is reduced from the reaction mass discharging/feeding tube to a first distillation column after an oximation reaction (16), a crude propylene oxide is obtained as a top liquid of the column, which contains propylene oxide, from a discharging tube of a top

liquid of a first distillation column (18) connected to the top section of the column. The obtained crude propylene oxide may be further purified by a known method or a method analogous thereto.

5 On the other hand, a solution containing acetonitrile, water, amides, oxazolines, and acetaldoxime formed by modification of acetaldehyde is obtained from a discharging tube of a bottom liquid of a first distillation column (17) connected to the bottom section of the column. In the case
10 of using a quinoid compound in the epoxidation reaction, a bottom liquid of the column is obtained as a quinoid compound-containing solution.

[0095]

 Then, in a second distillation column denoted by the
15 reference numeral (7) in Fig. 1 (hereinafter sometimes referred to as a second distillation column (7)) as one of embodiments of the specific second distillation column, by feeding a solution containing acetonitrile, water, amides, oxazolines, and acetaldoxime formed by modification of
20 acetaldehyde from a discharging tube of a bottom liquid of a first distillation column (17), acetonitrile is obtained from a discharging tube of a top liquid of a second distillation column denoted by the reference numeral (20) in Fig. 1 connected to the top section of the column
25 (hereinafter sometimes referred to as a discharging tube of a top liquid of a second distillation column (20)).

On the other hand, a solution containing water, amides, oxazolines, and acetaldoxime formed by modification of acetaldehyde is obtained from a discharging tube of a bottom liquid of a second distillation column denoted by the reference numeral (19) in Fig. 1 connected to the bottom section of the column (hereinafter sometimes referred to as a discharging tube of a bottom liquid of a second distillation column (19)).

[0096]

In the second distillation column, the theoretical plate number is within a range from 1 to 100. Regarding distillation conditions, for example, the temperature is within a range from 0°C to 300°C, the pressure is within a range from 0.005 MPa to 10 MPa, and the reflux ratio is within a range from 0.001 to 10.

[0097]

Acetonitrile (the composition of acetonitrile depends on distillation column pressure conditions and is usually within a range from 50/50 to 100/0 (acetonitrile/water: weight ratio)) obtained from the discharging tube of a top liquid of a second distillation column (20) connected to the top section of the column may be directly recycled to the epoxidation reaction, or may be further purified by a known method or a method analogous thereto.

[0098]

The oximation reaction in the second obtaining method

of the present invention will be described in more detail below.

As mentioned above, the second obtaining method of the present invention is composed of the recovery step and the separation/removal step. The separation/removal step does not include the process based on the epoxidation reaction, and only includes the process based on the oximation reaction.

It is possible to exemplify, as one of embodiments of the recovery step, the step of recovering propylene oxide existing in the reaction mass which is obtained by feeding, as a liquid gas, a reaction mass obtained by reacting the main raw materials into a gas-liquid separator, and then separating into a reaction mass as a liquid part and a gas as a gas part under a pressure which is the same as or lower than that obtained in the reaction.

It is possible to preferably exemplify, as another embodiment, an embodiment in which the separation/removal step is the step of distilling a reaction mass before removing acetaldoxime, and the distillation step includes the step of separating or removing by recovering a top liquid of the column, which contains acetonitrile, from a top section of a distillation column and also recovering a bottom liquid of the column, which contains acetaldoxime, from a bottom section of a distillation column.

[0099]

For example, an oximation reaction tank denoted by the reference numeral (5) in Fig. 2 (hereinafter sometimes referred to as an oximation reaction tank (5)) as one of embodiments of the specific apparatus for oximation reaction includes a paddle blade therein, and also includes a discharging tube of bottom liquid of a first distillation column (17) for continuously receiving a reaction mass from a first distillation column (crude propylene oxide separation column) (6), a hydroxylamine compound-containing solution feeding tube (15) for continuously receiving a hydroxylamine compound-containing solution and a reaction mass discharging/feeding tube to a second distillation column after an oximation reaction denoted by the reference numeral (16) in Fig. 2 (hereinafter sometimes referred to as reaction mass discharging/feeding tube to second distillation column after oximation reaction (16)) connected thereto. Then, a reaction mass containing acetonitrile in which the content of acetaldehyde is reduced is obtained from a reaction mass discharging/feeding tube to a second distillation column after an oximation reaction (16).

[0100]

Then, in a second distillation column denoted by the reference numeral (7) in Fig. 2 (i.e., second distillation column (7)) as one of embodiments of the specific second distillation column, by feeding a reaction mass containing

acetonitrile in which the content of acetaldehyde is reduced from a reaction mass discharging/feeding tube to a second distillation column after an oximation reaction (16), acetonitrile is obtained from a discharging tube of a top liquid of a second distillation column (20) connected to the top section of the column.

On the other hand, a solution containing water, amides, oxazolines, and acetaldoxime formed by modification of acetaldehyde is obtained from a discharging tube of a bottom liquid of a second distillation column (19) connected to the bottom section of the column.

[0101]

In the second distillation column, the theoretical plate number is within a range from 1 to 100. Regarding distillation conditions, for example, the temperature is within a range from 0°C to 300°C, the pressure is within a range from 0.005 MPa to 10 MPa, and the reflux ratio is within a range from 0.001 to 10.

[0102]

Acetonitrile (the composition of acetonitrile depends on distillation column pressure conditions and is usually within a range from 50/50 to 100/0 (acetonitrile/water: weight ratio)) obtained from the discharging tube of a top liquid of a second distillation column (20) connected to the top section of the column may be directly recycled to the epoxidation reaction, or may be further purified by a

known method or a method analogous thereto.

Examples

[0103]

5 The present invention will be described in more detail below by way of Examples.

[0104]

Example 1

<Preparation Method of Catalyst>

10 The Ti-MWW precursor used in Example 1 was prepared in the following manner.

 In an autoclave at room temperature (about 25°C) under an air atmosphere, 112 g of TBOT (tetra-n-butyl orthotitanate), 565 g of boric acid and 410 g of fumed
15 silica (cab-o-sil M7D) were dissolved in a mixture of 899 g of piperidine and 2,402 g of pure water while stirring to prepare a gel, and then the gel was aged in the autoclave for 1.5 hours.

 After the temperature of the obtained aged substance
20 was raised while stirring over 8 hours in a state where the autoclave is closed, hydrothermal synthesis was carried out by maintaining at 160°C for 120 hours to obtain a suspension. The obtained suspension was filtered and then the separated filter cake was washed with water until the
25 pH of the filtrate reached about 10.

 Then, the obtained filter cake was dried at 50°C to

obtain a white powder in a state of still containing water. To 15 g of the obtained powder, 750 mL of 2N nitric acid was added and then the obtained mixture was heated under reflux for 20 hours. The heated mixture was filtered and
5 then the separated filter cake was washed with water until the filtrate becomes nearly neutral.

Then, the obtained filter cake was sufficiently dried at 50°C to obtain 11 g of a white powder. The obtained white powder was subjected to the measurement of an X-ray
10 diffraction pattern by an X-ray diffractometer using copper K-alpha radiation. As a result, it was confirmed that the white powder is a Ti-MWW precursor. The content of titanium determined by ICP spectrometry was 1.6% by weight.

The Ti-MWW precursor thus obtained was further fired
15 at 530°C for 6 hours. The obtained fired product (27 g) was dissolved in an autoclave at room temperature under an air atmosphere while stirring with a mixture of 23 g of piperidine and 45 g of pure water to prepare a gel, and then the gel was aged for 1.5 hours.

20 After the temperature of the obtained aged substance was raised while stirring over 4 hours in a state where the autoclave is closed, hydrothermal synthesis was carried out by maintaining at 160°C for 16 hours to obtain a suspension. The obtained suspension was filtered and the separated
25 filter cake was washed with water until the pH of the filtrate reached about 9.

Then, the obtained filter cake was vacuum-dried at 150°C for 4 hours to obtain 26 g of a white powder. The obtained white powder was subjected to the measurement of an X-ray diffraction pattern by an X-ray diffractometer using copper K-alpha radiation. As a result, it was confirmed that the white powder has a MWW precursor structure. The content of Ti determined by ICP spectrometry was 1.67% by weight.

As a Ti-MWW precursor to be used in an epoxidation reaction in the subsequent step, a precursor treated in advance with hydrogen peroxide was used. Namely, a treated substance, obtained by treating 2.28 g of a Ti-MWW precursor powder with about 80 cc of a solution of water/acetonitrile = 20/80 (weight ratio) containing 0.1% by weight of hydrogen peroxide, at room temperature for 1 hour, was filtered and then the separated filter cake was recovered and the filter cake was used in the epoxidation reaction in the subsequent step.

[0105]

<Obtaining Method of the Present Invention: Epoxidation Reaction>

In the presence of both the titanosilicate catalyst prepared above and a catalyst in which a noble metal catalyst is supported on a carrier, hydrogen was reacted with oxygen in the reaction system in which hydrogen, oxygen and propylene are fed, thereby generating hydrogen

peroxide, and then an epoxidation reaction of producing propylene oxide by reacting the thus generated hydrogen peroxide with propylene was carried out.

Specifically, (i) 131 g of acetonitrile water at a weight ratio (water/acetonitrile) of 30/70, (ii) 2.28 g of the Ti-MWW precursor obtained in Example 1, and (iii) 1.06 g of a catalyst in which 1% by weight of palladium is supported on activated carbon (hereinafter sometimes referred to as a "palladium-supported activated carbon catalyst") were charged in a 300 cc autoclave equipped with a jacket and the pressure was adjusted to an absolute pressure of 4 MPa using nitrogen, and then the temperature in the autoclave was adjusted to 50°C by circulating hot water into the jacket. (i) a mixed gas with the composition of 3.7% by volume of hydrogen, 3.4% by volume of oxygen and 92.9% by volume of nitrogen (281 L (normal state)/hour), (ii) acetonitrile water (a weight ratio water/acetonitrile is 30/70) containing 0.7 mmol/kg of anthraquinone and 3.0 mmol/kg of diammonium hydrogen phosphate (90 g/hour), and (iii) a propylene solution (36 g/hour) were continuously fed in the autoclave. During the epoxidation reaction, the reaction temperature was controlled to 50°C and the reaction pressure was controlled to 4 MPa.

During the epoxidation reaction, a reaction mass obtained by removing both a Ti-MWW precursor and a

palladium-supported activated carbon catalyst through filtration using a sintered filter is subjected to gas-liquid separation under a normal pressure using a gas-liquid separation tank, whereby, a liquid component and a gas component were continuously extracted from the gas-liquid separation tank while separating.

After 8 hours have passed since the beginning of the epoxidation reaction, propylene oxide, propylene glycol and acetaldehyde contained in the extracted liquid component were analyzed by gas chromatography and liquid chromatography. As a result, the concentration of propylene oxide in the extracted liquid component increased to 9.8% by weight, and the concentration of propylene glycol increased to 0.1% by weight. Furthermore, the concentration of acetaldehyde (ACH) in the above component was 4 ppm by weight.

[0106]

Example 2

<Preparation of Mixture Containing Acetaldehyde under Assumption of Reaction Mass>

As a mixture corresponding to the liquid component obtained in Example 1, 80 g of an aqueous acetonitrile solution (weight ratio, acetonitrile/water = 66/34) containing acetaldehyde (ACH) in the concentration of 41 ppm by weight, propylene glycol in the concentration of 0.38% by weight, anthraquinone (a compound corresponding to

a quinone compound) in the concentration of 15 ppm by weight and diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$, a compound corresponding to a buffer agent) in the concentration of 39 ppm by weight was prepared.

5 [0107]

<Obtaining Method of the Present Invention: Oximation Reaction>

A mixture, obtained by adding 10% by weight of hydroxyamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) water to the mixture containing acetaldehyde prepared above so that hydroxyamine/acetaldehyde (mol/mol) becomes the value described in Table 1, was stirred at 70°C. The test results relating to retention of acetaldehyde (ACH) in the mixture at each lapsed time, assuming that retention of acetaldehyde (ACH) in the mixture immediately after mixing hydroxyamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) with acetaldehyde (ACH) is 100, are shown in Table 2. In Table 2, the results of a test (Comparative Example) carried out in the same manner, except that hydroxyamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) is not mixed, are also shown.

As is apparent from Table 1, it was confirmed that retention of acetaldehyde (ACH) in the mixture is reduced to 3% within 2.5 hours. The product formed as a result of reduction was acetaldoxime.

25 [0108]

Table 1

Elapsed time (hr)	The present invention (hydroxylamine hydrochloride is used)				Comparative Example (hydroxylamine hydrochloride is not used)
	NH ₂ OH/ACH (mol/mol)	ACH (ppm)	Product (ppm)	ACH retention (%)	ACH retention (%)
0	0	41	0	100	100
0.5	1.0	5	40	11	90
1	1.0	4	41	11	89
2	1.0	5	42	11	-
2.5	1.7	1	46	3	85

[0109]

Example 3 (Preparation of Mixture Containing Acetaldehyde under Assumption of Reaction Mass)

As a mixture corresponding to the liquid component obtained in Example 1, 80 g of an aqueous acetonitrile solution (weight ratio, acetonitrile/water = 66/34) containing acetaldehyde (ACH) in the concentration of 28 ppm by weight, propylene glycol in the concentration of 0.38% by weight, anthraquinone (a compound corresponding to a quinone compound) in the concentration of 15 ppm by weight and diammonium hydrogen phosphate ((NH₄)₂HPO₄, a compound corresponding to a buffer agent) in the concentration of 39 ppm by weight was prepared.

[0110]

<Obtaining Method of the Present Invention: Oximation Reaction>

A mixture, obtained by adding 5% by weight of hydroxyamine sulfate ((NH₂OH)₂·H₂SO₄) water to the mixture containing acetaldehyde prepared above so that

hydroxyamine/acetaldehyde (mol/mol) becomes the value described in Table 2, was stirred at 70°C. The test results relating to retention of acetaldehyde (ACH) in the mixture at each lapsed time, assuming that retention of acetaldehyde (ACH) in the mixture immediately after mixing hydroxyamine sulfate ((NH₂OH)₂·H₂SO₄) with acetaldehyde (ACH) is 100, are shown in Table 3. In Table 3, the results of a test (Comparative Example) carried out in the same manner, except that hydroxyamine sulfate ((NH₂OH)₂·H₂SO₄) is not mixed, are also shown.

As is apparent from Table 2, it was confirmed that retention of acetaldehyde (ACH) in the mixture is reduced to 8% within 1 hour. The product formed as a result of reduction was acetaldoxime.

[0111]

Table 2

Elapsed time (hr)	The present invention (hydroxylamine hydrochloride is used)				Comparative Example (hydroxylamine hydrochloride is not used)
	NH ₂ OH/ACH (mol/mol)	ACH (ppm)	Product (ppm)	ACH retention (%)	ACH retention (%)
0	0	28	0	100	100
0.5	1.2	8	29	28	90
1	1.9	2	37	8	89

[0112]

Example 3

<Preparation of Mixture Containing Acetaldehyde under Assumption of Reaction Mass>

As a mixture corresponding to the liquid component obtained in Example 1, 80 g of an aqueous acetonitrile solution (weight ratio acetonitrile/water = 59/30) containing acetaldehyde (ACH) in the concentration of 28 ppm by weight, propylene oxide in the concentration of 10.5 by weight, anthraquinone (a compound corresponding to a quinone compound) in the concentration of 15 ppm by weight and diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$, a compound corresponding to a buffer agent) in the concentration of 40 ppm by weight was prepared.

[0113]

<Obtaining Method of the Present Invention: Oximation Reaction>

A mixture, obtained by adding 5% by weight of hydroxyamine sulfate ($(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$) water to the mixture containing acetaldehyde prepared above so that hydroxyamine/acetaldehyde (mol/mol) becomes the value described in Table 3, was stirred at 70°C. The test results relating to retention of acetaldehyde (ACH) in the mixture at each lapsed time, assuming that retention of acetaldehyde (ACH) in the mixture immediately after mixing hydroxyamine sulfate ($(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$) with acetaldehyde (ACH) is 100, are shown in Table 4. In Table 4, the results of a test (Comparative Example) carried out in the same manner, except that hydroxyamine sulfate ($(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$) is not mixed, are also shown.

As is apparent from Table 3, it was confirmed that retention of acetaldehyde (ACH) in the mixture is reduced to 7% within 0.5 hour. On the other hand, it was also confirmed that propylene oxide (PO) is almost maintained and PG is not formed. The product formed as a result of reduction was acetaldoxime.

[0114]

Table 3

Elapsed time (hr)	The present invention (hydroxylamine hydrochloride is used)						Comparative Example (hydroxylamine hydrochloride is not used)		
	NH ₂ OH/ACH (mol/mol)	ACH (ppm)	Product (ppm)	ACH retention (%)	PO (wt%)	PG (wt%)	ACH retention (%)	PO (wt%)	PG (wt%)
0	0	28	0	100	10.56	0.00	100	10.23	0.01
0.5	2.1	2	37	7	10.05	0.01	90	-	-
1	-	-	-	-	-	-	89	10.22	0.02
1.5	2.1	3	36	11	10.06	0.02	-	-	-
2	-	-	-	-	-	-	-	10.17	0.03
2.5	2.1	3	35	11	10.04	0.04	85	-	-
3	-	-	-	-	-	-	-	9.98	0.04

10 Industrial Applicability

[0115]

According to the present invention, it becomes possible to provide a method for obtaining propylene oxide in which the content of acetaldehyde is reduced by enabling the removal of acetaldehyde.

Description of Reference Numerals

[0116]

(1) to (3): Epoxidation reaction tank

20 (4): Gas-liquid separation tank

(5): Oximation reaction tank

(6): First distillation column (Crude propylene oxide separation column)

(7): Second distillation column (Acetonitrile solvent separation column)

(9) Feeding tube of raw material of epoxidation reaction

(10) to (13): Epoxidation reaction mass discharging/feeding tube

(14): Reaction mass discharging tube after gas separation

(15): Hydroxylamine compound-containing solution feeding tube

(16): Reaction mass discharging/feeding tube to first distillation column after oximation reaction (Fig. 1), Reaction mass discharging/feeding tube to second

distillation column after oximation reaction (Fig. 2)

(17): Discharging tube of bottom liquid of first distillation column

(18): Discharging tube of top liquid of first distillation column

(19): Discharging tube of bottom liquid of second distillation column

(20): Discharging tube of top liquid of second distillation column

CLAIMS

1. A method for obtaining propylene oxide, which comprises steps of:

5 mixing a hydroxylamine compound in a reaction mass which is obtained by reacting both raw materials of (a) hydrogen peroxide, or hydrogen and oxygen, and (b) propylene in an acetonitrile-containing solvent in the presence of a catalyst, thereby entirely or partially
10 converting acetaldehyde contained in the reaction mass into acetaldoxime, and then separating or removing the acetaldoxime from the reaction mass; and
 recovering the reaction mass obtained by the former step or propylene oxide existing in the reaction mass.

15

2. The method for obtaining propylene oxide according to claim 1, wherein the separation/removal step is a step of mixing a hydroxylamine compound in the reaction mass, which is obtained by feeding, as a liquid gas, a reaction
20 mass obtained by reacting the both raw materials into a gas-liquid separator, and separating into a reaction mass as a liquid part and a gas as a gas part under a pressure which is the same as or lower than that obtained in the reaction, thereby entirely or partially converting
25 acetaldehyde contained in the reaction mass into acetaldoxime, and then separating or removing the

acetaldoxime from the reaction mass.

3. The method for obtaining propylene oxide according to claim 1 or 2, wherein the hydroxylamine compound is
5 hydroxylamine sulfate or hydroxylamine hydrochloride.

4. The method for obtaining propylene oxide according to claim 1 or 2, wherein the separation/removal step and the recovery step are allowed to proceed simultaneously.
10

5. The method for obtaining propylene oxide according to claim 4, wherein the separation/removal step and the recovery step are steps of distilling a reaction mass before removing acetaldoxime, and the distillation step
15 includes a step of separating or removing by recovering a top liquid of a distillation column, which contains propylene oxide, from a top section of the column and also recovering a bottom liquid of the column, which contains acetaldoxime and acetonitrile, from a bottom section of the
20 column.

6. A method for obtaining propylene oxide, which comprises steps of:

recovering propylene oxide existing in a reaction mass
25 which is obtained by reacting both raw materials of (a) hydrogen peroxide, or hydrogen and oxygen, and (b)

propylene in an acetonitrile-containing solvent in the presence of a catalyst; and

mixing a hydroxylamine compound in the reaction mass obtained after recovering propylene oxide by the former step, thereby entirely or partially converting acetaldehyde contained in the reaction mass into acetaldoxime, and then separating or removing the acetaldoxime from the reaction mass.

7. The method for obtaining propylene oxide according to claim 6, wherein the recovery step is a step of recovering propylene oxide existing in the reaction mass which is obtained by feeding, as a liquid gas, a reaction mass obtained by reacting the both raw materials into a gas-liquid separator, and separating into a reaction mass as a liquid part and a gas as a gas part under a pressure which is the same as or lower than that obtained in the reaction.

8. The method for obtaining propylene oxide according to claim 6 or 7, wherein the hydroxylamine compound is hydroxylamine sulfate or hydroxylamine hydrochloride.

9. The method for obtaining propylene oxide according to any one of claims 6 to 8, wherein the separation/removal step is a step of distilling a reaction mass before

removing acetaldoxime, and the distillation step includes a step of separating or removing by recovering a top liquid of a distillation column, which contains acetonitrile, from a top section of the column and also recovering a bottom liquid of the column, which contains acetaldoxime, from a bottom section of the column.

10. The method for obtaining propylene oxide according to any one of claims 1 to 9, wherein the catalyst is titanosilicate catalyst and also the raw material (a) is hydrogen peroxide.

11. The method for obtaining propylene oxide according to any one of claims 1 to 9, wherein the catalyst includes both a titanosilicate catalyst and a catalyst obtained by supporting palladium on a carrier, and the raw material (a) includes hydrogen and oxygen.

12. The method for obtaining propylene oxide according to claim 11, wherein the noble metal catalyst is palladium.

13. The method for obtaining propylene oxide according to claim 10 or 11, wherein the titanosilicate catalyst is a Ti-MWW precursor.

1/2

Fig.1

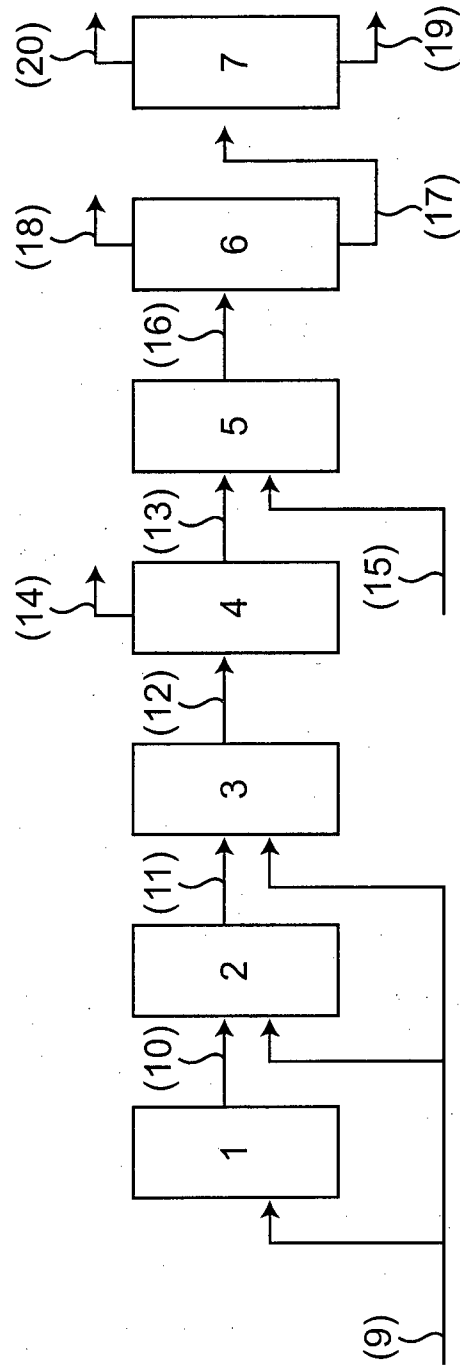
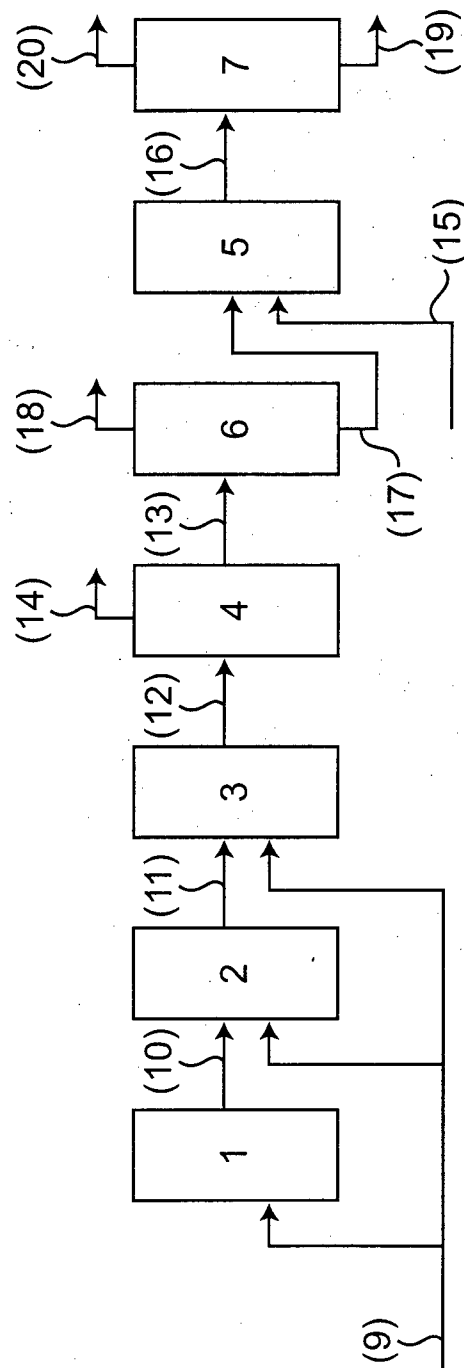


Fig.2



INTERNATIONAL SEARCH REPORT

International application No
PCT/JP2012/059946

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07D303/04 C07D301/03
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 424 332 A1 (DEGUSSA [DE]; UHDE GMBH [DE]) 2 June 2004 (2004-06-02) paragraphs [0013], [0019] -----	1-13
A	EP 0 557 116 A1 (ARCO CHEM TECH [US]) 25 August 1993 (1993-08-25) the whole document -----	1-13

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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