

SPECIFICATION

[Title of Invention]

Method for producing alkylene oxide adduct

5 [Technical Field]

The present invention relates to a method for producing an alkylene oxide adduct, which enables easy separation and elimination of a catalyst and a by-product from the target product.

10 [Background Art]

Polyoxyalkylene type nonionic surfactants prepared by adding alkylene oxide to an active hydrogen containing compound such as a higher alcohol, higher amine or the like, and a higher fatty acid alkyl ester are widely used in a variety of applications including the step of washing, emulsification or dispersion. The reason for this is that
15 the hydrophilic – lipophilic balance (HLB) can freely be controlled by appropriately adjusting the addition number of moles of alkylene oxide serving as the hydrophilic group.

To prepare the above-mentioned alkylene oxide adduct, there is proposed a
20 method of using a solid catalyst for alkoxylation, in particular, an alkali-modified solid catalyst for alkoxylation to obtain a reaction product with a narrow distribution of the addition number of moles of alkylene oxide. However, when the solid catalyst is used, by-products such as high-molecular weight polyethylene glycol with a weight-average molecular weight of 10,000 or more and the like are generated in the reaction liquid,
25 which may unfavorably cause a problem in separating the desired alkylene oxide adduct from the solid catalyst. To be more specific, there occur the problems, such as clogging of the filter cloth used for filtering out the solid catalyst, decreasing of the yield resulting from the alkylene oxide adduct to be mingled with the so-called “waste cake” that is separated for disposal, and a turbidity appearing in the target alkylene
30 oxide adduct. It is necessary to solve those problems.

In light of the above-mentioned problems, a method of bringing an acryl polymer as the aggregation promoter and water into contact with a crude alkylene oxide adduct is proposed for efficiently separating and eliminating the catalyst (JP 9-262456 A). This method allows the polyalkylene glycol generated as a by-product to aggregate, thereby easily separating the polyalkylene glycol from the solid catalyst for alkoxylation and readily removing the polyalkylene glycol therefrom. According to this method, however, the filtration performance is not always satisfactory in the crude adduct where the addition number of moles of alkylene oxide is large, which is accompanied with increased generation of a high-molecular weight polyalkylene glycol. In addition, there are still another disadvantages of increasing waste and increasing cost.

Also, a method of adjusting the pH and the water content of the crude alkylene oxide adduct is disclosed in WO 2008/078768. In this method, however, there also remain the problems that the filtration needs excessive time and the amount of waste filtration cake is large.

[Summary of Invention]

[Technical Problem]

An object of the invention is to provide a method for producing an alkylene oxide adduct using a solid catalyst for alkoxylation, wherein the catalyst and the polyalkylene glycol generated as the by-product can be efficiently separated and eliminated from the desired alkylene oxide adduct.

[Solution to Problem]

As a result of extensive studies, the inventors of the present invention found that the solid catalyst and the polyalkylene glycol can efficiently form aggregates by adding an aqueous solution of organic carboxylic acid to the crude alkylene oxide adduct while heating the crude adduct obtained through the reaction using a solid catalyst for alkoxylation, and then cooling and appropriately adjusting the water content of the

crude adduct. Thus, the invention has been accomplished.

Namely, the invention provides a method for producing an alkylene oxide adduct, comprising the step (A) of adding an aqueous solution of organic carboxylic acid to a crude alkylene oxide adduct which is obtainable by adding alkylene oxide to an active hydrogen containing compound and/or a fatty acid alkyl ester in the presence of a solid catalyst for alkoxylation, to adjust the crude alkylene oxide adduct to pH5 to 7 when measured at 25°C with a concentration of 5 mass%, as maintaining the temperature of the crude alkylene oxide adduct in a range from 90 to 130°C inclusive; and the step (B) of adjusting the water content of the crude adduct to 8 mass% or more and 12 mass% or less, as controlling the temperature of the crude alkylene oxide adduct in a range from 50 to 80°C inclusive.

[Effects of Invention]

According to the invention, the solid catalyst and the by-product of polyalkylene glycol can be easily and efficiently separated and eliminated from the alkylene oxide adduct. This can reduce the amount of alkylene oxide adduct to be mingled with the waste, so that the yield of alkylene oxide adduct can be increased. At the same time, it becomes possible to obtain an alkylene oxide adduct having high clarity, with minimum solid catalyst and polyalkylene glycol remaining in the obtained alkylene oxide adduct.

[Description of Embodiments]

Step (A)

A crude alkylene oxide adduct is obtained by the addition reaction of an alkylene oxide to an active hydrogen containing compound and/or a fatty acid alkyl ester in the presence of a solid catalyst for alkoxylation.

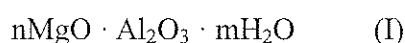
[Solid catalyst for alkoxylation]

The solid catalyst for alkoxylation used in the invention includes Al-Mg composite oxide catalysts, for example, magnesium oxide to which a metal ion is added

(JP 06-15038 B, JP 07-227540 A, JP 06-198169 A, JP 06-182206 A, and JP 05-170688 A); sintered hydrotalcite (JP 02-71841 A); aluminum hydroxide – magnesium sintered product (JP 08-268919 A) and the like. Those catalysts may be subjected to surface modification by alkali modification treatment (JP 08-169860 A and JP 08-169861 A).

5 In particular, when the alkali-modified catalyst is used for the reaction, the amount of unreacted fatty acid alkyl ester remaining in the reaction system can be reduced, and it is possible to obtain a reaction product with an extremely narrow distribution of the addition number of moles of alkylene oxide. In the invention, therefore, the surface modified aluminum hydroxide – magnesium sintered product subjected to alkali
10 modification treatment is preferably used as the catalyst.

There is no particular limitation on the aluminum hydroxide – magnesium sintered product. According to the application, any aluminum hydroxide – magnesium sintered product, for example, the one as described in JP 08-268919 A or the like may
15 appropriately be chosen. More specifically, aluminum – magnesium composite metal oxides represented by the following formula (I) can be used, which are obtainable by sintering a co-precipitate of aluminum hydroxide and magnesium hydroxide.



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In the formula (I), n and m is not particularly limited so long as the number is positive, and n may be in the range of 1 to 3, and especially, n of about 2.5 is preferably used; and m may appropriately be chosen according to the application.

25 As for the sintering conditions of catalyst, the sintering temperature may appropriately be chosen according to the application, and preferably be in the range of 400 to 950°C, more preferably 800 to 900°C in consideration of the development of catalytic activity and the control of the amount of generated by-products. The sintering time may appropriately be chosen, and usually be 2 to 4 hours when the
30 sintering process is carried out under the above-mentioned conditions.

When the sintering temperature is too low, the catalytic activity may not develop or the amount of generated by-products may unfavorably increase.

5 In contrast to this, excessively high sintering temperature reduces the specific surface area of the catalyst particles and induces the structural change of the aluminum – magnesium composite oxide, which may decrease the catalytic acid sites involved in the ring opening polymerization reaction of alkylene oxide to disadvantageously lower the reaction activity.

10 In other words, it is desirable to properly control the sintering conditions of catalyst from the two viewpoints, that is, maintaining high reaction activity and reducing the amount of generated by-products. For the proper control, the specific surface area of catalyst particles can be used as an index of the process control. In
15 addition to the above, the intensity of the acid sites on the solid surfaces that can be determined by ammonia adsorption or the like, and the degree of spinel formation that can be determined by analyzing the crystalline structure according to X-ray diffraction can also be used as the effective indexes.

20 When the specific surface area is used as the index of the properties of catalyst, the values of BET surface areas measured, for example, with a rapid surface area measuring instrument, model SA-1000 or the like (made by Sibata Scientific Technology Ltd.) may be used. The specific surface area of the catalyst particles may preferably be in the range of 100 to 200 m²/g.

25 The particle size of the catalyst particles is not particularly limited, but the mean particle size is usually in the range of 10 to 1,000 μm.

30 The mean particle size of the catalyst herein used means a value calculated as the median diameter from the determination with a laser scattering particle distribution

analyzer, model LA-920 (made by HORIBA Ltd.) using acetonitrile as a dispersion medium.

There is no particular limitation on the surface modified catalyst that is prepared
5 by subjecting the above-mentioned aluminum hydroxide - magnesium sintered product
to alkali modification treatment. According to the application, any surface-modified
catalyst, for example, as also described in JP 08-169860 A and JP 08-169861 A may
appropriately be chosen. More specifically, the above-mentioned aluminum hydroxide
- magnesium sintered product may be surface-modified with a metal hydroxide or metal
10 alkoxide to form modified aluminum hydroxide - magnesium sintered catalyst. As the
metal hydroxide, hydroxides of alkali metals or alkaline earth metals are preferable, and
in particular, sodium hydroxide and potassium hydroxide are more preferable. As the
metal alkoxide, alkoxides of alkali metals or alkaline earth metals are preferable, and in
particular, sodium alkoxide and potassium alkoxide are preferable. The alkoxide may
15 preferably have 1 to 4 carbon atoms.

For completing the alkali modification treatment, for example, the catalyst may
be modified with the hydroxide or alkoxide of alkali metals or alkaline earth metals
prior to the use in the reaction. Alternatively, in a reaction vessel for alkoxylation the
20 fatty acid alkyl ester as the raw material may be mixed with the metal hydroxide or
metal alkoxide to modify the catalyst in the raw material. In other words, the alkali
modification may be conducted in the course of preparation of the catalyst, or the alkali
modification may be conducted by using an alkali in the course of the addition reaction.

25 The above-mentioned catalyst may be used alone or two or more catalysts may be
used in combination.

The particle size of the catalyst is not particularly limited, but usually subject to
changes. Specifically, the catalyst particles may disintegrate as a result of the heat of
30 reaction accumulated within the inside of catalyst particles, generation of high

molecular weight by-products, sudden change of pressure, application of mechanical shearing by the movement of stirring impeller or the like.

Further, for enhancing the catalyst activity, a polyol is sometimes added to the reaction mixture to micronize the catalyst, which will be described later. Therefore, the particle size of the catalyst incorporated in the crude product after completion of the reaction can be, for example, 0.1 to 500 μm when expressed as the mean diameter.

The amount of catalyst used is not particularly limited so long as the reaction may properly proceed, and may appropriately be chosen according to the activity of the employed catalyst and the like. The amount of catalyst may preferably be in the range of 0.01 to 5 mass%, more preferably 0.03 to 1 mass%, and most preferably 0.05 to 0.2 mass%, based on the total mass of the above-mentioned reaction materials (i.e., fatty acid alkyl ester and alkylene oxide). With the amount of the catalyst being adjusted within the preferable range as mentioned above, the reaction can properly proceed.

[Active hydrogen containing compound]

The active hydrogen containing compound for use in the invention is not particularly limited, and may appropriately be chosen depending on the purpose. For example, alcohols, amines, amides, phenols and derivatives thereof, thiols and derivatives thereof and the like can be employed. In particular, alcohols are preferable, and alcohols represented by the following formula (1) are more preferable.



In the formula (1), R_1 is not particularly limited, and may appropriately be chosen according to the properties required of the intended product. For example, straight-chain or branched alkyl groups, straight-chain or branched alkenyl groups and the like can be listed. R_1 may have any number of carbon atoms. The number of carbon atoms may appropriately be chosen according to the purpose, but preferably in

the range of 1 to 40, more preferably 3 to 30 and most preferably 6 to 22.

Specific examples of the alcohol include saturated or unsaturated higher aliphatic primary alcohols having a straight-chain alkyl group with 8 to 22 carbon atoms, such as
5 n-octanol, n-decanol, n-dodecanol, n-tetradecanol, n-hexadecanol, n-octadecanol, oleyl alcohol, eicosanol, behenol, nonanol, undecanol, tridecanol and the like; primary alcohols having branched alkyl group, such as 2-ethyl hexanol, Guerbet alcohols having 16 to 36 carbon atoms and the like; secondary alcohols such as 2-octanol, 2-decanol, 2-dodecanol and the like; and benzyl alcohol and the like.

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Specific examples of the amine include primary and secondary amines having a saturated or unsaturated alkyl group with 8 to 24 carbon atoms, such as octylamine, dioctylamine, laurylamine, dilaurylamine, stearylamine, distearylamine and the like; polyamines such as ethylenediamine, diethylenetriamine and the like.

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Specific examples of the amide include alkanolamides having 12 to 18 carbon atoms, such as lauric acid monoethanolamide, lauric acid diethanolamide and the like.

Of the above-mentioned active hydrogen containing compounds, straight-chain or
20 branched saturated or unsaturated alcohols with 8 to 22 carbon atoms are preferable.

[Fatty acid alkyl ester]

The fatty acid alkyl ester used in the invention is not particularly limited, and may appropriately be chosen according to the purpose. The above-mentioned fatty acid
25 esters are represented by the following formula (2):



wherein R_2 and R_3 are each a straight-chain or branched alkyl group or a straight-chain or branched alkenyl group.

30 R_2 may preferably have 1 to 40 carbon atoms, more preferably 3 to 30 carbon

atoms, and most preferably 5 to 21 carbon atoms. R_3 may preferably have 1 to 30 carbon atoms, more preferably 1 to 10 carbon atoms, and most preferably 1 to 4 carbon atoms.

5 The fatty acid alkyl ester may be used alone or in combination. As the fatty acid alkyl ester, triglyceride, that is, fatty acid ester of glycerin can also be used.

10 The amount of fatty acid alkyl ester is not particularly limited, and may appropriately be chosen depending on the desired amount of product, the amount of the employed catalyst and the amount of alkylene oxide which will be described later.

[Alkylene oxide]

15 The alkylene oxide used in the invention is not particularly limited so long as alkylene oxide adducts can be obtained through the reaction with the above-mentioned active hydrogen containing compound and/or fatty acid alkyl ester. The alkylene oxide may appropriately be chosen according to the application, and for example, alkylene oxides having 2 to 4 carbon atoms are preferred. Specifically, ethylene oxide, propylene oxide, butylene oxide and the like can be used, which may be used alone or in combination.

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[Crude alkylene oxide adduct]

25 To form an adduct in the invention, preferably 1 to 50 moles, more preferably 3 to 30 moles, and most preferably 5 to 20 moles of the alkylene oxide may be added to 1 mole of the active hydrogen containing compound and/or fatty acid alkyl ester. When the alkylene oxide adduct is used for a nonionic surfactant, the structure of adduct may preferably have a HLB of 3 to 20 when measured by the Griffin's method.

30 The amount of the above-mentioned alkylene oxide is not particularly limited, and may appropriately be chosen depending on the kind of fatty acid alkyl ester to be used, the properties required of the intended product and the like. With respect to one

mole of the above-mentioned fatty acid alkyl ester, the alkylene oxide may preferably be used in an amount of 1 to 50 moles, more preferably 3 to 30 moles, and most preferably 5 to 20 moles.

5 [Optional components that can be used for the addition reaction in step (A)]

In the reaction of step (A), a low molecular weight polyol may be added. The addition of the low molecular weight polyol to the reaction system can micronize the catalyst, thereby improving the catalyst activity.

10 Any polyol can be used without any restriction so long as the polyol has two or more hydroxyl groups in the molecule thereof and the effect of micronizing the catalyst can be obtained. For example, any compounds that can be uniformly emulsified or dispersed in the above-mentioned fatty acid alkyl ester may appropriately be chosen according to the application. Preferably, glycerin, ethylene glycol, diethylene glycol
15 and the like may be used. In particular, glycerin is preferred. The polyol may be used alone or in combination.

The amount of the above-mentioned polyol is not particularly limited, and may appropriately be chosen according to the application. For example, the polyol may be
20 used in an amount of 0.02 to 0.5 mass% of the total mass of the raw materials for the reaction (i.e., the active hydrogen containing compound and/or fatty acid alkyl ester, and alkylene oxide). In addition, the content of the polyol may preferably be 1.0 times or more, more preferably 1.25 times or more as much as the mass of the catalyst. It becomes possible to micronize the catalyst speedily and thoroughly by adjusting the
25 content of the polyol within the above-mentioned preferable range.

[Procedures and reaction conditions of step (A)]

The crude alkylene oxide adduct can be easily prepared from the above-mentioned raw materials by following the well-known procedures and reaction
30 conditions. The reaction temperature may preferably be 80 to 230°C, and the reaction

pressure, which depends on the reaction temperature, may preferably be 0 to 2 MPa, more preferably 0.2 to 0.8 MPa. When necessary, the addition reaction of alkylene oxide may be carried out under the condition of nitrogen dilution.

5 To conduct the above-mentioned reaction, for example, the active hydrogen containing compound and/or fatty acid alkyl ester and the solid catalyst for alkoxylation are placed into an autoclave, and then the alkylene oxide may be introduced into the reaction system in an atmosphere of nitrogen under the predetermined conditions of the reaction temperature and pressure.

10 [Addition of aqueous solution of organic carboxylic acid]

An aqueous solution of organic carboxylic acid is added to the crude alkylene oxide adduct which is maintained at 90°C or more and 130°C or less, to adjust the resultant mixture containing 5 mass% of the crude adduct to pH 5 to 7 when measured
15 at 25°C. In other words, the aqueous solution of organic carboxylic acid is added to the crude alkylene oxide adduct in such an amount that can obtain the pH value of 5 to 7 when the pH of the crude adduct is measured at the concentration of 5 mass% and the temperature of 25°C. The concentration of organic acid in the aqueous solution is not particularly limited, but preferably 3 to 20 mass%.

20 Preferable examples of the organic carboxylic acid include malic acid, lactic acid, citric acid, glycolic acid, acetic acid or hydrates thereof. In particular, malic acid, lactic acid, citric acid, glycolic acid, citric acid or the hydrates thereof are more preferable. Of the above, citric acid or hydrates thereof are most preferable. Those
25 acids may be used alone or in combination. Without wishing to be bound by any theory, the organic carboxylic acid is supposed to be adsorbed by the solid catalyst and the polyalkylene glycol generated as the by-product, thereby forming aggregates.

When the aqueous solution of organic carboxylic acid is added to the crude
30 adduct, the temperature of the crude adduct is maintained at 90°C or more and 130°C or

less, preferably at 100°C or more and 125°C or less. When the above-mentioned temperature is less than 90°C, the amount of waste will increase. The reason for this is considered that the adsorption of organic carboxylic acid on the solid catalyst may become insufficient. When the above-mentioned temperature exceeds 130°C, the increased vapor pressure of water will worsen the handling properties. The temperature of the aqueous solution of organic carboxylic acid to be added to the crude adduct is not particularly limited. When the organic carboxylic acid containing aqueous solution of less than 90°C is added to the crude adduct, the temperature of the crude adduct is temporarily decreased. However, even though the temperature of the crude adduct is temporarily not within the above-mentioned range (90 to 130°C), the amount of waste and the handling properties are not so much influenced.

Generally, the organic carboxylic acid containing aqueous solution may be added to the crude alkylene oxide adduct over a period of 5 to 30 minutes, preferably 10 to 20 minutes.

When the pH of the crude adduct is less than 5 after the addition of organic carboxylic acid containing aqueous solution, the adsorption of the organic carboxylic acid on the solid catalyst is not sufficient, so that the amount of waste will increase. When the above-mentioned pH exceeds 7, insufficient adsorption of the organic carboxylic acid on the solid catalyst will also increase the amount of waste.

After addition of the aqueous solution of organic carboxylic acid, stirring may be conducted to uniformly mix the crude adduct with the organic carboxylic acid. In this case, the stirring may be continued for five minutes or more, more preferably 5 to 60 minutes, which may vary depending on the stirring velocity. When the stirring time is less than five minutes, the organic carboxylic acid aqueous solution and the crude alkylene oxide adduct may not be mixed well, and therefore, the solid catalyst and the polyalkylene glycol may not be fully separated by centrifugal separation. On the other hand, even if the stirring continues more than 60 minutes, further stirring effect cannot

be expected, and the processing time will unfavorably extend.

The stirring may be conducted using a stirring tank. As for the stirring conditions, general stirrers including paddles, propellers, turbine blades, anchor
5 agitators and the like can be employed. The stirring velocity may be freely set so long as the whole contents can be stirred, but the power requirements for stirring per unit volume may be in the range of 0.1 to 0.9 kW/m³.

During the stirring operation, the mixture of the aqueous solution of organic
10 carboxylic acid and the crude alkylene oxide adduct is maintained at 90°C or more and 130°C or less, preferably 100°C or more and 120°C or less.

[Step (B)]

Subsequently, the temperature is adjusted to 50°C or more and 80°C or less,
15 preferably 60°C or more and 75°C or less, and then the water content of the crude adduct is adjusted to 8 mass% or more and 12 mass% or less. With the temperature being within the above-mentioned range, once the crude adduct is cooled to 80°C, the water content may be adjusted with continuous cooling. Alternatively, after the crude adduct is cooled to 80°C, the water content may be adjusted with the cooling operation
20 being once stopped.

When the temperature is less than 50°C, the formation of aggregates of the solid catalyst and the polyalkylene glycol cannot proceed thoroughly, so that it becomes difficult to fully eliminate the solid catalyst and the polyalkylene glycol, and there
25 remains the problem of milky turbidity. When the temperature exceeds 80°C, the polyalkylene glycol will dissolve, so that the polyalkylene glycol cannot be sufficiently eliminated from the alkylene oxide adduct, which will also cause the problem of milky turbidity.

30 It does not matter how long it takes to cool the crude adduct of 90 to 130°C to a

temperature ranging from 50 to 80°C. Usually, it takes 30 to 60 minutes.

The crude adduct may be cooled to the predetermined temperature by leaving the crude adduct or allowing the cooling water to flow into a jacket or inner coil of the stirring tank, for example.

The water content is adjusted to 8 to 12 mass%, preferably 9 to 11 mass%. When the water content is less than 8 mass%, aggregation of the high molecular weight polyalkylene glycol does not proceed, so that the polyalkylene glycol cannot satisfactorily be separated and eliminated from the alkylene oxide adduct. Therefore, the turbidity of the adduct will increase. When the water content exceeds 12 mass%, the polyalkylene glycol will dissolve in the adduct, so that the polyalkylene glycol cannot be sufficiently separated and eliminated from the alkylene oxide adduct. Thus, there will appear a milky turbidity in the resultant adduct.

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The water content of the crude adduct is usually less than 8 mass% after the crude adduct is cooled to a temperature in the range of 50 to 80°C. Therefore, the water content of the crude adduct may be adjusted by addition of water. The water used in the invention is not particularly limited, and for example, distilled water and deionized water may be used. The water content may usually be adjusted over a period of 5 to 30 minutes, preferably 10 to 20 minutes.

In the invention, the water content may be determined by Karl Fischer method, using a liquid of the alkylene oxide crude adduct obtained after the organic carboxylic acid aqueous solution is added. It is possible to use a Karl Fischer titrator, model AQV-7, made by Hiranuma Sangyo Co., Ltd., or the like.

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[Optional step]

Subsequently to the step (B), a centrifugal separation or conventional filtration step may be conducted to separate and eliminate the aggregates of the catalyst for

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alkoxylation, those of the by-product polyalkylene glycol or those of the mixture thereof from the alkylene oxide adduct. Prior to the removal of the catalyst and the like from the alkylene oxide adduct, the alkylene oxide adduct may be stirred. In this case, the temperature of the alkylene oxide adduct may preferably be 30 to 60°C, more preferably 40 to 60°C. The stirring time may preferably be 10 to 120 minutes, more preferably 30 to 60 minutes. The stirring velocity may be freely set so long as the whole contents can be mixed, but the power requirements for stirring per unit volume may be in the range of 0.1 to 0.9 kW/m³. The general stirring equipment as mentioned in the step (A) is usable for stirring.

The appearance of the alkylene oxide adduct thus obtained is clear and homogeneous.

The clarity of the alkylene oxide adduct can be evaluated by determining the turbidity at 50°C. The turbidity may be determined using an integrating sphere type turbidimeter, model SEP-PT-760D (made by Mitsubishi Chemical Corporation) or the like. The turbidity is expressed in the unit of ppm, and the higher the level of the clarity is, the smaller the value of turbidity is.

The turbidity of the obtained alkylene oxide adduct is preferably less than 2 ppm, more preferably less than 1.5 ppm, and most preferably less than 1 ppm when measured at 50°C. When the turbidity exceeds 2 ppm, a slight milky turbidity can be visually recognized. When such an alkylene oxide adduct is incorporated in a detergent and the like, the appearance of the resultant product may be impaired by turbidity.

The homogeneity of the alkylene oxide adduct is visually inspected, with the adduct being placed in a transparent container at 50°C. The appearance free of any precipitate or suspended matter is evaluated as homogeneous. The alkylene oxide adduct having precipitate and suspended matter therein may cause the problem of the appearance of the final products, such as turbidity and the presence of precipitates when

incorporated in the products such as detergent and the like.

When the separation is conducted by the conventional filtering operation, filter paper such as two-layered filter composed of cellulose and polyester, metal mesh type
5 filter or the like may be used to complete the filtration under reduced pressure or increased pressure at 35 to 100°C, especially 40 to 85°C. Preferably, some filter aid may be used to improve the filtering capability. Any filter aid known to the skilled persons in this art can be used. For example, as the diatom earth of amorphous silicic acid containing as the main component SiO_2 in an amount of 80 to 95%, Radiolite #100,
10 Radiolite #200, Radiolite #500, Radiolite #600, Radiolite #900, Zemlite Super M, Zemlite Super 1, Zemlite Super 56, Zemlite Super 2, Celite 501, Celite 503, Celite 535, Celite 545, Hyflo Super Cel, Standard Super Cel, Filter Cel and the like can be employed. As aluminum silicate containing as the main component SiO_2 in an amount of about 70%, for example, Topco #31, Topco #34 and the like can be employed. As
15 the cellulose filter aid, KC Flock, SW40, BW20, BW40, BW100, BW200, BNB20 and the like can be employed. Those can be used alone or in combination. The amount of filter aid may preferably be in the range of about 0.05 to 5 mass%, especially 0.1 to 2 mass%, of the total mass of the crude adduct.

20 In the course of filtration, the temperature of the crude adduct may preferably be in the range of 40 to 60°C, more preferably 45 or more and 55°C or less. When the above-mentioned temperature exceeds 60°C, the solubility of polyalkylene glycol in the alkylene oxide adduct will be higher, so that it becomes difficult to satisfactorily separate the polyalkylene glycol, and therefore there may sometimes appear a milky
25 turbidity in the resultant alkylene oxide adduct. When the temperature is less than 40°C, the viscosity of the crude alkylene oxide adduct will increase, which may cause insufficient separation and removal of the solid catalyst and the polyalkylene glycol, and therefore there may appear a milky turbidity in the obtained alkylene oxide adduct.

30 When the centrifugal separator is employed, a decanter centrifuge is preferred

because the separated solid components can be continuously discharged.

The decanter centrifuge comprises an outer rotational cylinder and a screw conveyor, which are driven to rotate at high speeds in the same direction with a slight
5 difference in rotational speed. When the target liquid is fed into the rotational cylinder, the aggregates having higher specific gravity are settled against the inner wall of the rotational cylinder by the centrifugal force. When separated from the liquid component, the aggregates are finally scraped from the wall by the movement of the screw conveyer and discharged from the centrifuge.

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The decanter centrifuges are classified into vertical ones and horizontal ones according to the orientation of the rotational cylinder, both of which can be used in the invention. The feeding system of liquid into the decanter centrifuge has two types, parallel current type and counter current type. In the former type, the liquid feeding
15 direction is the same as the liquid flow direction in the rotational cylinder, and in the latter type, the liquid feeding direction is opposite to the liquid flow direction. Both types are capable of separation in the invention.

As one example of the decanter centrifuge, a model BDN made by Tomoe
20 Engineering Co., Ltd., can be used in the invention.

In the course of centrifugal separation, the temperature of the crude adduct may preferably be in the range of 40 to 60°C, more preferably 45 to 55°C.

25 When the above-mentioned temperature exceeds 60°C, the solubility of polyalkylene glycol in the alkylene oxide adduct will be higher, so that it becomes difficult to satisfactorily separate the polyalkylene glycol, and therefore there may sometimes appear a milky turbidity in the resultant alkylene oxide adduct. When the temperature is less than 40°C, the viscosity of the crude alkylene oxide adduct will
30 increase, which may cause insufficient separation of the solid catalyst and the

polyalkylene glycol and therefore there may sometimes appear a milky turbidity in the obtained alkylene oxide adduct.

As for the operating conditions of the decanter centrifuge, the centrifugal force
5 may be preferably in the range of 1500 to 3500 G, more preferably 1500 to 3000 G. Too small centrifugal force cannot fully remove the aggregates of the solid catalyst and polyalkylene oxide from the alkylene oxide adduct. As a result, the alkylene oxide adduct may become turbid or contaminated with some precipitates. On the other hand, when the centrifugal force is excessively large, the aggregates are strongly pushed
10 against the inner wall of the rotational cylinder, with the result that the aggregates adhering to the inner wall cannot be smoothly discharged by the screw conveyor, and the resultant liquid separated may be contaminated with some precipitates.

In the decanter centrifuge, the difference in rotational speed between the
15 rotational cylinder and the screw conveyor may preferably be in the range of 5 to 20 rpm, more preferably 10 to 15 rpm. When the difference in rotational speed is too small, the retention time of the solid matter separated in the rotational cylinder is extended, and therefore the ratio of the solid matter to the liquid in the rotational cylinder becomes large and the likelihood of contamination of the liquid with
20 precipitates may increase.

On the other hand, when the difference in the rotational speed is too large, the retention time of the solid matter separated in the rotational cylinder is reduced, and therefore the ratio of the liquid to be contained in the solid matter becomes high, which
25 may sometimes increase the amount of waste.

If air bubbles are mixed in the alkylene oxide adduct through the solid-liquid separation by the decanter centrifuge, a deaeration step may be further provided for removing the air bubbles using a deaerator. The deaerator may be chosen from a
30 variety of deaerators such as vacuum deaerator, pressure degassing apparatus, stirring

defoaming apparatus, a centrifugal deaerator and the like. In particular, a defoaming – degassing pump, ASP type (made by Yokota Manufacturing Co., Ltd.) is preferred in the invention because continuous processing can be achieved, and the pump can also serve as the transfer pump.

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[Examples]

The invention will now be explained more specifically by referring to the following examples and comparative examples, but the present invention is not intended to be limited to these examples.

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[Preparation of catalyst]

Aluminum hydroxide – magnesium having a chemical composition of $2.5\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot \text{mH}_2\text{O}$ (Kyoward 300, made by Kyowa Chemical Industry C., Ltd.) was allowed to pass through a sintering zone of 880°C over a period of three hours in a tunnel-shaped kiln. Thus, magnesium – aluminum composite metal oxide catalyst was obtained in the form of particles.

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Example 1

[Step (A)]

In a 15-kL stirring reaction vessel, 1840 kg of methyl laurate (Pastel M12, made by Lion Corporation), 660 kg of methyl myristate (Pastel M14, made by Lion Corporation), 10 kg of the composite metal oxide catalyst prepared in the above, and 12.5 kg of glycerin as the polyol (in an amount of 0.5 mass% of the total mass of methyl laurate and methyl myristate) were placed, and then 0.5 kg of potassium hydroxide was added, followed by stirring for 10 minutes, so that the catalyst was treated by alkali modification.

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Then, the atmosphere in the reaction vessel was replaced with nitrogen and heated to 100°C with stirring, and the mixture in the vessel was subjected to dehydration for 30 minutes under reduced pressure of 1.3 kPa or less.

30

Then, with the reaction system being heated to 180°C, 7480 kg of ethylene oxide (15 times more than the fatty acid methyl esters in terms of mole) was introduced into the reaction system under the conditions that the upper limit of the pressure was set to
5 0.49 MPa.

After the reaction system was subjected to aging for 0.5 hours, the reaction system was cooled to 80°C, thereby obtaining 10,000 kg of a crude ethylene oxide adduct (where the average addition number of moles of ethylene oxide was 15). The
10 crude product contained 0.9 mass % of polyethylene glycol as a by-product.

The average addition number of moles of ethylene oxide was determined by high performance liquid chromatography (HPLC). (The measuring conditions were as follows. Column: Inertsil C8 made by GL Sciences Inc. (particle size of 5 µm, inner
15 diameter of 4.6 mm, length of 250 mm) Mobile phase: acetonitrile/water (60/40 by volume), 1 mL/min. Refractive index detector: L-7490, made by Hitachi, Ltd. Column temperature: 15°C. Injection volume: 200 µL)

The concentration of the by-product polyethylene glycol contained in the crude
20 product was determined by gel permeation chromatography (GPC). (The measuring conditions were as follows. Column: Shodex GF-310HQ, Mobile phase: acetonitrile/water (45/55 by volume), 1 mL/min. Refractive index detector: RID-6A, made by Shimadzu Corporation. Column temperature: 30°C. Injection volume: 200 µL)

25 In 121 kg of purified water of room temperature, 11 kg of citric acid monohydrate was dissolved to prepare an aqueous solution of citric acid monohydrate.

Thereafter, 9,000 kg of the above-mentioned crude product was placed into a
30 15-kL stirring tank and heated to 120°C with stirring. With the temperature of the

crude product in the stirring tank being maintained at 120°C, the aqueous solution of citric acid monohydrate was added over a period of 10 minutes with stirring (power requirements for stirring per unit volume: about 0.5 kw/m³). Immediately after completion of the addition of the aqueous solution of citric acid monohydrate, the temperature of the crude product was 118°C. A small portion of the crude product was sampled from the stirring tank and diluted 20 times with water (to obtain a concentration of 5 mass%) and the pH of the sample product was measured at 25°C. The pH was found to be 5.8.

The crude product in the stirring tank was heated to 120°C, and then stirred for 10 minutes with the temperature being controlled within the range of 120±2°C.

[Step (B)]

Thereafter, the above-mentioned crude product was cooled to 70°C, to which 879 kg of purified water of ordinary temperature was added in order to adjust the water content of the crude product to 10%.

Subsequently, the crude product was cooled to 50°C, and then stirred for 60 minutes with the temperature of the crude product being maintained at 50°C, using a pitched blade paddle impeller (the power requirements for stirring per unit volume: about 0.5 kw/m³). The above-mentioned process made the by-product polyethylene glycol and the catalyst aggregate to form solid matters dispersed in the crude product.

The solid matters formed by aggregating the polyethylene glycol and the catalyst were removed from the above-mentioned crude product by centrifugal separation.

To be specific, the crude product of 50°C obtained through the step (B) was fed to a decanter centrifuge (Model BDN-34 with a rotational cylinder having a radius of 0.18 m, made by Tomoe Engineering Co., Ltd.) at a feed rate of 1000 kg/hour. The number of revolutions of the rotational cylinder was set to 3250 rpm (centrifugal separation

effect: 2100 G), and the difference in the rotational speed between the rotational cylinder and the screw conveyor was set to 15 rpm. The crude product was subjected to centrifugal separation under the above-mentioned conditions to separate the solid matters from the liquid, both of which were separately discharged from the centrifugal separator.

The separated liquid discharged from the centrifugal separator was subjected to continuous deaeration treatment at a throughput rate of 10,000 kg/hour using a defoaming – degassing pump, model ASP-0310S, made by Yokota Manufacturing Co., Ltd. The air bubbles were thus removed from the separated liquid, so that 9790 kg of a purified product (ethylene oxide adduct diluted with water) was obtained in a 97.9% yield.

The solid matters (including the aggregates of solid catalyst and polyethylene glycol and the water content) separated by the centrifugal separator weighed 210 kg. The amount ratio of the solid matters (i.e., waste) thus separated out was 2.1% by mass with respect to the resultant purified product.

The purified product was recognized as a homogeneous product free of precipitates and suspended matters visible to the naked eye. The turbidity of the purified product at 50°C was 0.1 ppm, which demonstrated the obtained product was clear.

Examples 2 to 5

The procedures of Example 1 were repeated except that citric acid used in the step (A) was replaced by glycolic acid, malic acid, lactic acid, and acetic acid respectively in Examples 2, 3, 4 and 5.

Similar to the alkylene oxide adduct obtained in Example 1, the resultant alkylene oxide adducts were free of precipitates and suspended matters visible to the naked eye,

and showed small values of turbidity. The liquids were thus evaluated as acceptable in terms of the homogeneity and the clarity.

Examples 6 and 7

5 The procedures of Example 1 were repeated except that the temperature of the crude adduct was changed to 90°C and 130°C respectively in Examples 6 and 7 when the citric acid was added in the step (A).

10 Similar to the alkylene oxide adduct obtained in Example 1, the resultant alkylene oxide adducts were free of precipitates and suspended matters visible to the naked eye, and showed small values of turbidity. The liquids were thus evaluated as acceptable in terms of the homogeneity and the clarity.

Examples 8 and 9

15 The procedures of Example 1 were repeated except that the pH was adjusted to 5.0 and 7.0 in the step (A) respectively in Examples 8 and 9.

20 Similar to the alkylene oxide adduct obtained in Example 1, the resultant alkylene oxide adducts were free of precipitates and suspended matters visible to the naked eye, and showed small values of turbidity. The liquids were thus evaluated as acceptable in terms of the homogeneity and the clarity.

Examples 10 and 11

25 The procedures of Example 1 were repeated except that the water content was adjusted to 8% and 12% in the step (B) respectively in Examples 10 and 11.

30 Similar to the alkylene oxide adduct obtained in Example 1, the resultant alkylene oxide adducts were free of precipitates and suspended matters visible to the naked eye, and showed small values of turbidity. The liquids were thus evaluated as acceptable in terms of the homogeneity and the clarity.

Examples 12 and 13

The procedures of Example 1 were repeated except that the temperature of the crude adduct was changed to 50°C and 130°C respectively in Examples 12 and 13 when
5 water was added in the step (B).

Similar to the alkylene oxide adduct obtained in Example 1, the resultant alkylene oxide adducts were free of precipitates and suspended matters visible to the naked eye, and showed small values of turbidity. The liquids were thus evaluated as acceptable in
10 terms of the homogeneity and the clarity.

Examples 14 and 15

The procedures of Example 1 were repeated except that the temperature of the crude adduct was changed to 90°C when the citric acid was added in the step (A), and
15 the water content was adjusted to 8% and 12% in the step (B) respectively in Examples 14 and 15.

Similar to the alkylene oxide adduct obtained in Example 1, the resultant alkylene oxide adducts were free of precipitates and suspended matters visible to the naked eye,
20 and showed small values of turbidity. The liquids were thus evaluated as acceptable in terms of the homogeneity and the clarity.

Example 16

The procedures of Example 1 were repeated except that the temperature of the
25 crude adduct was changed to 130°C when the citric acid was added and the pH was adjusted to 5.0 in the step (A), and the water content was adjusted to 8% in the step (B).

Similar to the alkylene oxide adduct obtained in Example 1, the resultant alkylene oxide adduct was free of precipitates and suspended matters visible to the naked eye,
30 and showed a small value of turbidity. The liquid was thus evaluated as acceptable in

terms of the homogeneity and the clarity.

Example 17

The procedures of Example 1 were repeated except that the citric acid was
5 replaced by lactic acid and the pH was adjusted to 5.0 in the step (B), and the water
content was adjusted to 12% in the step (B).

Similar to the alkylene oxide adduct obtained in Example 1, the resultant alkylene
oxide adduct was free of precipitates and suspended matters visible to the naked eye,
10 and showed a small value of turbidity. The liquid was thus evaluated as acceptable in
terms of the homogeneity and the clarity.

Example 18

The procedures of Example 1 were repeated except that the citric acid was
15 replaced by lactic acid and the temperature of the crude adduct was changed to 90°C
when the lactic acid was added, and the pH was adjusted to 7.0 in the step (A), and the
water content was adjusted to 8% in the step (B). Similar to the alkylene oxide adduct
obtained in Example 1, the resultant alkylene oxide adduct was free of precipitates and
suspended matters visible to the naked eye, and showed a small value of turbidity. The
20 liquid was thus evaluated as acceptable in terms of the homogeneity and the clarity.

Example 19

The procedures of Example 1 were repeated except that the citric acid was
replaced by lactic acid and the temperature of the crude adduct was changed to 90°C
25 when the lactic acid was added, and the pH was adjusted to 7.0 in the step (A), and the
water content was adjusted to 12% at 50°C in the step (B).

Similar to the alkylene oxide adduct of Example 1, the resultant alkylene oxide
adduct was free of precipitates and suspended matters visible to the naked eye, and
30 showed small values of turbidity. The homogeneity and the clarity of the liquid were

thus evaluated as acceptable.

Comparative Example 1

The procedures of Example 1 were repeated except that the temperature of the
5 crude adduct was changed to 80°C when the citric acid was added in the step (A).

Although the turbidity was less than 1.5 ppm, which demonstrated the clarity was acceptable, the amount ratio of the waste was as high as 3.0 mass% or more of the purified product.

10

Comparative Examples 2 and 3

The procedures of Example 1 were repeated except that the pH was adjusted to 4.0 and 8.0 in the step (B), respectively in Comparative Examples 2 and 3.

15 In both Comparative Examples, the turbidity exceeded 5 ppm, which demonstrated the liquid was turbid and the clarity was unacceptable, and in addition, the amount ratio of the waste was as high as 3.0 mass% or more of the purified product.

Comparative Example 4

20 The procedures of Example 1 were repeated except that the organic carboxylic acid was replaced by hydrochloric acid in the step (A).

The turbidity exceeded 2 ppm, which demonstrated the clarity was unacceptable, and in addition, the amount ratio of the waste was as high as 2.5 mass% or more of the
25 purified product.

Comparative Examples 5 and 6

The procedures of Example 1 were repeated except that the water content was adjusted to 5% and 15% in the step (B), respectively in Comparative Examples 5 and 6.

30 In both Comparative Examples, the turbidity exceeded 5 ppm, which

demonstrated the liquid was turbid and the clarity was unacceptable, and in addition, the amount ratio of the waste was as high as 2.5 mass% or more of the purified product.

The alkylene adduct was diluted with deionized water until the concentration reached 5 mass%, and the pH was measured at 25°C by use of a pH meter (model HM-30V, made by DKK-TOA Corporation).

The water content was determined using a Karl Fischer titrator (model AQV-7, made by Hiranuma Sangyo Co., Ltd.).

The clarity of the obtained alkylene oxide adduct (as a purified product) was assessed by measuring the turbidity (unit: ppm) at 50°C with an integrating sphere type turbidimeter (model SEP-PT-760D, made by Mitsubishi Chemical Corporation). The smaller value of turbidity was indicated, the higher clarity of the product was recognized and the better separation of the solid catalyst and the polyalkylene glycol was demonstrated. The turbidity was rated on the five scales shown below.

ooo: turbidity of less than 1 ppm

oo: turbidity of 1 ppm or more and less than 1.5 ppm

o: turbidity of 1.5 ppm or more and less than 2 ppm

Δ: turbidity of 2 ppm or more and less than 5 ppm

x: turbidity of 5 ppm or more

The centrifugal force in the step of centrifugal separation was calculated in accordance with the following numerical formula:

$$\text{Centrifugal force (G)} = (\pi^2 \times R \times N^2) / (900 \times g)$$

wherein π represents the ratio of the circumference of a circle to its diameter,

R represents the inner radius (m) of the rotational cylinder,

N represents the number of revolutions (rpm) of the rotational cylinder, and

g represents the gravitational acceleration (m/s^2).

The productivity was assessed by the yield of the obtained alkylene oxide adduct (as a purified product), and rated on the four scales as shown below.

- 5 oo: yield of 97.7 wt.% or more
 o: yield of 97.5 wt.% or more and less than 97.7 wt.%
 Δ: yield of 97 wt.% or more and less than 97.5 wt.%
 x: yield of less than 97 wt.%

- 10 The results of Examples are shown in Tables 1 and 2, and those of Comparative Examples are shown in Table 3.

Table 1

		Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9
Step (A)	Organic carboxylic acid	citric acid	glycolic acid	malic acid	lactic acid	acetic acid	citric acid	citric acid	citric acid	citric acid
	Temp. (°C) of crude product when aqueous organic carboxylic acid solution was added	120	120	120	120	120	90	130	120	120
	pH (measured at 25°C with a concentration of 5%) just after completion of addition of aqueous organic carboxylic acid solution	5.8	5.8	5.8	5.8	5.8	5.8	5.8	5.0	7.0
Step (B)	Water content (%) of crude product after water content adjustment	10	10	10	10	10	10	10	10	10
	Temp. (°C) of crude product when water was added	70	70	70	70	70	70	70	70	70
Properties of resultant purified alkylene oxide product	Turbidity (50°C)	ooo	oo	oo	oo	o	oo	oo	o	o
Evaluation of productivity	Amount ratio of waste (based on purified product)	oo	oo	oo	oo	oo	o	oo	o	o

Table 2

		Ex. 10	Ex. 11	Ex. 12	Ex. 13	Ex. 14	Ex. 15	Ex. 16	Ex. 17	Ex. 18	Ex. 19
Step (A)	Organic carboxylic acid	citric acid	citric acid	citric acid	citric acid	citric acid	citric acid	citric acid	lactic acid	lactic acid	lactic acid
	Temp. (°C) of crude product when aqueous organic carboxylic acid solution was added	120	120	120	120	90	90	130	120	90	120
	pH (measured at 25°C with a concentration of 5%) just after completion of addition of aqueous organic carboxylic acid solution	6.0	6.0	6.0	6.0	6.0	6.0	5.0	5.0	7.0	7.0
Step (B)	Water content (%) of crude product after water content adjustment	8	12	10	10	8	12	8	12	8	12
	Temp. (°C) of crude product when water was added	70	70	50	80	70	70	70	70	70	50
Properties of resultant purified alkylene oxide product	Turbidity (50°C)	o	o	o	o	o	o	o	o	o	o
Evaluation of productivity	Amount ratio of waste (based on purified product)	oo	oo	oo	oo	o	o	o	o	o	o

Table 3

		Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6	Comp. Ex. 7	Comp. Ex. 8
Step (A)	Organic carboxylic acid	citric acid	citric acid	citric acid	hydrochloric acid	citric acid	citric acid	citric acid	citric acid
	Temp. (°C) of crude product when aqueous organic carboxylic acid solution was added	80	120	120	120	120	120	120	120
	pH (measured at 25°C with a concentration of 5%) just after completion of addition of aqueous organic carboxylic acid solution	6.0	4.0	8.0	6.0	6.0	6.0	6.0	6.0
Step (B)	Water content (%) of crude product after water content adjustment	10	10	10	10	5	15	10	10
	Temp. (°C) of crude product when water was added	70	70	70	70	70	70	40	90
Properties of resultant purified alkylene oxide product	Turbidity (50°C)	oo	x	x	Δ	x	x	x	Δ
Evaluation of productivity	Amount ratio of waste (based on purified product)	Δ	x	x	Δ	Δ	Δ	o	o

CLAIMS

1. A method for producing an alkylene oxide adduct, comprising:

the step (A) of adding an aqueous solution of organic carboxylic acid to a crude alkylene oxide adduct which is obtainable by adding alkylene oxide to an active hydrogen containing compound and/or a fatty acid alkyl ester in the presence of a solid catalyst for alkoxylation, to adjust the crude alkylene oxide adduct to pH5 to 7 when measured at 25°C with a concentration of 5 mass%, as maintaining the temperature of the crude alkylene oxide adduct in a range from 90 to 130°C inclusive; and

the step (B) of adjusting the water content of the crude adduct to 8 mass% or more and 12 mass% or less, as controlling the temperature of the crude alkylene oxide adduct in a range from 50 to 80°C inclusive.

2. The method of claim 1, wherein the temperature of the crude alkylene oxide adduct is maintained in a range from 100 to 125°C inclusive in the step (A).

3. The method of claim 1 or 2, wherein the organic carboxylic acid is at least one selected from the group consisting of malic acid, lactic acid, citric acid, glycolic acid and hydrates thereof.

4. The method of any one of claims 1 to 3, wherein the temperature of the crude alkylene oxide adduct is controlled in a range from 60 to 75°C inclusive in the step (B).

5. The method of any one of claims 1 to 4, wherein the water content of the crude adduct is adjusted to 8 mass% or more and 12 mass% or less by addition of water in the step (B).

6. The method of any one of claims 1 to 5, further comprising the step of subjecting the alkylene oxide adduct to centrifugal separation or filtration.