

DESCRIPTION

ALKOXYLATION CATALYST, METHOD FOR PRODUCING CATALYST, AND
METHOD FOR PRODUCING FATTY ACID ALKYL ESTER ALKOXYLATE USING
5 CATALYST

TECHNICAL FIELD

[0001]

The present invention relates to an alkoxylation catalyst, a method for producing
10 the catalyst, and a method for producing a fatty acid alkyl ester alkoxyate using the
catalyst.

Priority is claimed on Japanese Patent Application No. 2012-092161, filed April
13, 2012, the content of which is incorporated herein by reference.

15 BACKGROUND ART

[0002]

An organic compound having an active hydrogen or an alkylene oxide adduct as
a derivative of the organic compound has been widely used as a solvent, a surfactant or a
variety of chemical intermediates. In particular, an alkylene oxide adduct obtainable by
20 adding an alkylene oxide such as an ethylene oxide or a propylene oxide to an alcohol, a
fatty acid, a fatty acid alkyl ester, an amine, an alkylphenol, or the like has been widely
used as a non-ionic surfactant.

For example, a fatty acid alkyl ester alkoxyate obtainable by adding an alkylene
oxide to a fatty acid alkyl ester, and an alcohol alkoxyate obtainable by adding an
25 alkylene oxide to an alcohol have been frequently used as a detergent component for a

liquid detergent.

[0003]

As a method for producing an alkylene oxide adduct, a method in which an alkylene oxide is added to a fatty acid alkyl ester or an alcohol in the presence of an alkoxylation catalyst can be mentioned.

[0004]

With respect to a non-ionic surfactant composed of an alkylene oxide adduct, a non-ionic surfactant having narrow distribution of the addition mole number has more benefits such as a high foaming property than a non-ionic surfactant having wide distribution of the addition mole number.

Furthermore, in the production of a non-ionic surfactant, if a large amount of an unreacted raw material is allowed to remain, detergency would be deteriorated, and therefore, the unreacted raw material should be removed, which makes the manufacturing process complicated.

On the other hand, in the case where a large amount of a non-ionic surfactant having narrow distribution of the addition mole number is blended to a liquid detergent, the fluidity of the liquid detergent is likely to be deteriorated. For the reason above, with respect to a non-ionic surfactant composed of an alkylene oxide adduct, a non-ionic surfactant having narrow distribution of the addition mole number and a non-ionic surfactant having wide distribution of the addition mole number are appropriately used for the purpose.

In general, as an alkoxylation catalyst, a homogeneous catalyst such as an acid or a base and/or a heterogeneous catalyst such as a solid metal are used. The addition reaction (i.e., alkoxylation reaction) of an alkylene oxide to a fatty acid alkyl ester having no active hydrogen in the molecule thereof cannot proceed when using sodium hydroxide

as a catalyst. For this reason, in the addition reaction of an alkylene oxide to a fatty acid alkyl ester, the heterogeneous catalyst should be used as a catalyst.

As the heterogeneous catalyst, a calcined aluminum magnesium hydroxide catalyst having the surface subjected to modification using a metal hydroxide or a metal alkoxide has been proposed (see Patent Document 1).

Alternatively, an alkoxylation catalyst containing a mixture of a calcium salt of a carboxylic acid and/or a calcium salt of hydroxycarboxylic acid, sulphuric acid, and an alcohol and/or an ester, or containing a reaction product of the mixture has been proposed (see Patent Document 2).

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PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0005]

[Patent Document 1] Japanese Patent No. 2940852

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[Patent Document 2] International Publication No. 02/38269

DISCLOSURE OF INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0006]

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However, in the case where an alkoxylation reaction of a fatty acid alkyl ester is conducted using the catalyst disclosed in Patent Document 1 or 2, by-products such as polyethylene glycol (having a weight-average molecular weight of 10,000 or more measured in accordance with a gel permeation chromatography method) are generated.

There is a problem that, when a fatty acid alkyl ester alkoxylate containing a

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high-molecular polyethylene glycol is used in a liquid detergent, the liquid detergent is

likely to be clouded. For this reason, a step of removing by-products from the obtained alkylene oxide adduct is required, which makes the manufacturing process complicated. Furthermore, there is a problem that, when a large amount of by-products is generated, the amount of waste is increased.

5 Taking these problems into consideration, the present invention has an object to provide an alkoxylation catalyst capable of reducing the production amount of by-products.

MEANS FOR SOLVING THE PROBLEMS

10 [0007]

The present invention has the following aspects.

[1] An alkoxylation catalyst for use in a reaction of alkoxylation of a fatty acid alkyl ester represented by general formula (I) shown below, the alkoxylation catalyst being formed when a component (B) that is at least one member selected from the group
15 consisting of an alkaline-earth metal salt of a carboxylic acid, an alkaline-earth metal salt of a hydroxycarboxylic acid, an oxide of an alkaline-earth metal and a hydroxide of an alkaline-earth metal and a component (C) that is sulphuric acid are reacted in a component (A) that is a liquid dispersion medium, wherein the molar ratio represented by the component (C)/the component (B) is 0.8 to 1:

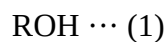
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$$R^{11}COOR^{12} \cdots (I)$$

in the formula (I), R^{11} is a hydrocarbon group having 1 to 40 carbon atoms; and R^{12} is a linear alkyl group having 1 to 3 carbon atoms.

[2] The alkoxylation catalyst according to [1], wherein

the component (A) is at least one member selected from the group consisting of
25 an alcohol represented by general formula (1) shown below, an alkylene oxide adduct of

the alcohol, a fatty acid alkyl ester represented by general formula (2) shown below, an alkylene oxide adduct of the fatty acid alkyl ester, a fatty acid represented by general formula (3) shown below and an alkylene oxide adduct of the fatty acid:



5 in the formula (1), R is a hydrocarbon group having 3 to 18 carbon atoms;



in the formula (2), R^1 is a hydrocarbon group having 3 to 18 carbon atoms; and

R^2 is a linear alkyl group having 1 to 3 carbon atoms; and



10 in the formula (3), R^3 is a hydrocarbon group having 3 to 18 carbon atoms.

[3] The alkoxylation catalyst according to [1] or [2], wherein

the molar ratio represented by the component (C)/the component (B) is 0.8 to less than 1.

[4] The alkoxylation catalyst according to [1] or [2], wherein

15 the molar ratio represented by the component (C)/the component (B) is 0.9 to less than 1.

[5] The alkoxylation catalyst according to [1] or [2], wherein

the molar ratio represented by the component (C)/the component (B) is 0.9 to 0.98.

20 [6] The alkoxylation catalyst according to [1] or [2], wherein

the molar ratio represented by the component (C)/the component (B) is 0.93 to 0.98.

[0008]

[7] A method for producing an alkoxylation catalyst of [1] or [2], including:

25 mixing a component (B) that is at least one member selected from the group

consisting of an alkaline-earth metal salt of a carboxylic acid, an alkaline-earth metal salt of a hydroxycarboxylic acid, an oxide of an alkaline-earth metal and a hydroxide of an alkaline-earth metal and a component (C) that is sulphuric acid are reacted in a component (A) that is a liquid dispersion medium, wherein

5 the molar ratio represented by the component (C)/the component (B) is 0.8 to 1.

[8] The method for producing an alkoxylation catalyst according to [7], wherein the weight ratio represented by [the component (B) + the component (C)]/the component (A) is 1 to 1/3.

[9] The method for producing an alkoxylation catalyst according to [7] or [8],
10 wherein

the molar ratio represented by the component (C)/the component (B) is 0.8 to less than 1.

[10] The method for producing an alkoxylation catalyst according to [7] or [8],
wherein

15 the molar ratio represented by the component (C)/the component (B) is 0.9 to less than 1.

[11] The method for producing an alkoxylation catalyst according to [7] or [8],
wherein

the molar ratio represented by the component (C)/the component (B) is 0.9 to
20 0.98.

[12] The method for producing an alkoxylation catalyst according to [7] or [8],
wherein

the molar ratio represented by the component (C)/the component (B) is 0.93 to 0.98.

25 [0009]

[13] A method for producing a fatty acid alkyl ester alkoxylate, including adding an alkylene oxide to a fatty acid alkyl ester in the presence of an alkoxylation catalyst of any one of [1] to [6].

5 [14] A method for producing a fatty acid alkyl ester alkoxylate, including adding an alkylene oxide to a fatty acid alkyl ester in the presence of a polyhydric alcohol and an alkoxylation catalyst of any one of [1] to [6].

[15] The method for producing a fatty acid alkyl ester alkoxylate according to [14], wherein the polyhydric alcohol is one member selected from the group consisting of an alkylene glycol, a polyalkylene glycol and glycerin.

10 [16] The method for producing a fatty acid alkyl ester alkoxylate according to [15], wherein the polyhydric alcohol is one member selected from the group consisting of ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol and glycerin.

EFFECTS OF THE INVENTION

15 [0010]

According to the alkoxylation catalyst of the present invention, the production amount of by-products is reduced.

BEST MODE FOR CARRYING OUT THE INVENTION

20 [0011]

(Alkoxylation Catalyst)

An alkoxylation catalyst of the present invention is an alkoxylation catalyst used for an alkoxylation reaction of a fatty acid alkyl ester and is obtainable by reacting at least one member selected from the group consisting of an alkaline-earth metal salt of a carboxylic acid, an alkaline-earth metal salt of a hydroxycarboxylic acid, an oxide of an

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alkaline-earth metal and a hydroxide of an alkaline-earth metal (hereafter, sometimes referred to as “component (B)”) and sulphuric acid (hereafter, sometimes referred to as “component (C)”) in a liquid dispersion medium (hereafter, sometimes referred to as “component (A)”). That is, the alkoxylation catalyst of the present invention contains a
5 reaction product of the component (B) and component (C) (an alkaline earth metal sulfate which is the main active component of the catalyst).

[0012]

The alkoxylation catalyst may be a dispersion liquid in which an alkaline earth metal sulfate is dispersed in the component (A), or a solid containing an alkaline earth
10 metal sulfate.

In the case where the alkoxylation catalyst is a dispersion liquid, the amount of alkaline earth metal sulfate in the dispersion liquid is not particularly limited, and is preferably 10 to 30% by weight.

[0013]

15 <Component (A)>

The component (A) is a liquid dispersion medium. The component (A) is not particularly limited, as long as the reaction between the component (B) and the component (C) can proceed while maintaining the fluidity without gelation during the production of the alkoxylation catalyst. With respect to the component (A), the term
20 “liquid” refers to a liquid state during a dispersing step and a mixing step described later.

In terms of increase productivity in a method for producing the alkoxylation catalyst described later, the component (A) is preferably in a liquid state at 30°C.

[0014]

As the component (A), at least one member selected from the group consisting
25 of an alcohol represented by general formula (1) shown below, an alkylene oxide adduct

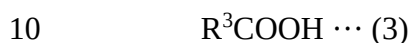
of the alcohol, a fatty acid alkyl ester represented by general formula (2) shown below, an alkylene oxide adduct of the fatty acid alkyl ester, a fatty acid represented by general formula (3) shown below and an alkylene oxide adduct of the fatty acid is preferably used.



[In the formula (1), R is a hydrocarbon group having 3 to 18 carbon atoms.]



[In the formula (2), R^1 is a hydrocarbon group having 3 to 18 carbon atoms; and R^2 is a linear alkyl group having 1 to 3 carbon atoms.]



[In the formula (3), R^3 is a hydrocarbon group having 3 to 18 carbon atoms.]

[0015]

In the formula (1), the number of carbon atoms is 3 to 18, preferably 3 to 12, and more preferably 3 to 8. When the number of carbon atoms is less than the lower limit of
15 the above-mentioned range, the viscosity of the component (A) is increased to be a gel state thereby reducing the fluidity thereof during the production of the alkoxylation catalyst, and the reaction between the component (B) and the component (C) is less likely to proceed. When the number of carbon atoms is greater than the upper limit of the above-mentioned range, the melting point is increased, which it is not suitable in the
20 dispersion medium.

R may be linear or branched.

R may be a saturated hydrocarbon group (alkyl group) or an unsaturated hydrocarbon group such as an alkenyl group.

Examples of alcohols represented by the aforementioned formula (1) include
25 primary alcohols such as 1-hexanol, n-octanol, n-decanol, n-dodecanol, n-tetradecanol,

n-hexadecanol, n-octadecanol, oleyl alcohol, nonanol, undecanol, tridecanol and the like; and secondary alcohols such as 2-ethylhexanol, 2-propanol, 2-octanol, 2-decanol, 2-dodecanol and the like. Among these, in terms of reducing the production amount of the high-molecular polyethylene glycol, 2-ethylhexanol is preferably used.

5 [0016]

With respect to an alkylene oxide adduct of the alcohol (i.e., alcohol alkoxyate), as the alkylene oxide to be added, an alkylene oxide having 2 to 3 carbon atoms can be mentioned.

The addition mole number of the alkylene oxide is preferably 1 to 7.

10 [0017]

In the aforementioned formula (2), the number of carbon atoms of R^1 is 3 to 18, and any number can be selected as long as there is good fluidity at a temperature during the production of alkoxylation catalyst.

R^1 may be linear or branched.

15 R^1 may be a saturated hydrocarbon group (alkyl group) or an unsaturated hydrocarbon group such as an alkenyl group.

[0018]

In the aforementioned formula (2), R^2 is preferably a linear alkyl group having 1 to 3 carbon atoms, and more preferably a methyl group having one carbon atom.

20 By ensuring the above-mentioned range, the melting point becomes low, and the fluidity becomes excellent under the temperature condition in the production of an alkoxylation catalyst.

[0019]

Examples of fatty acid alkyl esters represented by the aforementioned formula

25 (2) include fatty acid methyl esters such as methyl decanoate, methyl laurate, methyl

myristate and methyl oleate, and a mixture thereof.

[0020]

With respect to an alkylene oxide adduct of the fatty acid alkyl ester (i.e., alcohol alkoxyate of fatty acid alkyl ester), as the alkylene oxide to be added, an
5 alkylene oxide having 2 to 3 carbon atoms can be mentioned.

The addition mole number of the alkylene oxide is preferably 1 to 7.

[0021]

In the aforementioned formula (3), the number of carbon atoms of R^3 is 3 to 18, and any number can be selected as long as there is good fluidity at a temperature during
10 the production of alkoxylation catalyst.

R^3 may be linear or branched.

R^3 may be a saturated hydrocarbon group (alkyl group) or an unsaturated hydrocarbon group such as an alkenyl group.

Examples of fatty acids include octanoic acid, decanoic acid, lauric acid,
15 palmitoleic acid, oleic acid, linoleic acid, linolenic acid, and the like. Among these, oleic acid is preferably used.

[0022]

With respect to an alkylene oxide adduct of the fatty acid, as the alkylene oxide to be added, an alkylene oxide having 2 to 3 carbon atoms can be mentioned.

20 The addition mole number of the alkylene oxide is preferably 1 to 7.

[0023]

As the component (A), one type may be used, or two or more types may be used in combination.

[0024]

25 <Component (B)>

The component (B) is at least one member selected from the group consisting of an alkaline-earth metal salt of a carboxylic acid (hereafter, sometimes referred to as “component (b1)”), an alkaline-earth metal salt of a hydroxycarboxylic acid (hereafter, sometimes referred to as “component (b2)”), an oxide of an alkaline-earth metal (hereafter, sometimes referred to as “component (b3)”) and a hydroxide of an alkaline-earth metal (hereafter, sometimes referred to as “component (b4)”).

[0025]

Examples of the component (b1) include a calcium salt of carboxylic acid such as calcium acetate (e.g., calcium acetate nonhydrate, calcium acetate monohydrate), calcium formate, and the like; and a magnesium salt of carboxylic acid such as magnesium acetate, magnesium formate, and the like. Among these, in terms of enhancing the activity of the catalyst, a calcium salt of carboxylic acid is preferably used, and calcium acetate is more preferably used.

[0026]

Examples of the component (b2) include a calcium salt of hydroxycarboxylic acid such as calcium lactate, calcium tartrate, calcium citrate, calcium malate, and the like; and a magnesium salt of hydroxycarboxylic acid such as magnesium lactate, magnesium tartrate, magnesium citrate, magnesium malate, and the like. Among these, in terms of enhancing the activity of the catalyst, a calcium salt of hydroxycarboxylic acid is preferably used.

[0027]

Examples of the component (b3) include calcium oxide, magnesium oxide, and the like. Among these, calcium oxide is preferably used.

[0028]

Examples of the component (b4) include calcium hydroxide, magnesium

hydroxide, and the like. Among these, calcium hydroxide is preferably used.

[0029]

As the component (B), in terms of enhancing the activity of the catalyst and reducing the production amount of by-products, the component (b1) is preferably used, a
5 calcium salt of carboxylic acid is more preferably used, and calcium acetate is more preferably used.

As the component (B), one type may be used, or two or more types may be used in combination.

[0030]

10 <Component (C)>

The component (C) is sulphuric acid. As the component (C), dilute sulphuric acid or concentrated sulphuric acid may be used. In terms of exhibiting the activity of the catalyst stably, as the component (C), concentrated sulphuric acid (96% by weight or more) is preferably used.

15 [0031]

(Method for producing alkoxylation catalyst)

The method of producing an alkoxylation catalyst of the present invention is a method including: mixing the component (B) and the component (C) in the component (A).

20 As the method for producing an alkoxylation catalyst, a method including: a dispersing step in which the component (B) is dispersed in the component (A) to obtain a dispersed material; and a mixing step in which the component (C) is added to the obtained dispersed material to be mixed with the component (B).

[0032]

25 In the dispersing step, a reactor equipped with a mixing tank having a jacket and

a paddle stirring blade provided in the stirring tank is used, and the component (A) and the component (B) are fed into the reactor, followed by stirring.

[0033]

In the step, the temperature condition is not particularly limited, and for example,
5 room temperature (e.g., 5 to 35°C) can be applied. The temperature control in the stirring tank is conducted by flowing a heating medium (e.g., water) having an arbitrary temperature in the jacket.

In the step, the stirring time is not particularly limited, and is the time required to disperse the component (B) into the component (A) to be a substantially uniform
10 dispersion. The substantially uniform refers to a condition in which the component (B) is uniformly dispersed without aggregation detected by visual observation.

[0034]

In the mixing step, the component (C) is added to the dispersed material obtained in the dispersing step, followed by mixing the component (B) with the
15 component (C) to generate a reaction product of the component (B) and component (C) (i.e., to generate an alkaline earth metal sulfate which is the main active component of the catalyst), thereby obtaining an alkoxylation catalyst in which the active component of the catalyst is dispersed in the component (A).

In the step, the stirring method is not particularly limited, and for example, a
20 method can be preferably employed, in which the component (C) is added to the dispersed material in a dropwise matter while stirring the dispersed material in the stirring tank.

[0035]

The molar ratio represented by the component (C)/the component (B) (hereafter,
25 sometimes referred to as “C/B ratio”) is 0.8 to 1, preferably 0.8 to less than 1, more

preferably 0.9 to less than 1, still more preferably 0.9 to 0.98, and particularly preferably 0.93 to 0.98.

When the C/B ratio is at least as large as the lower limit of the above-mentioned range, in the obtainable alkoxylation catalyst, the production amount of by-products
5 during the production process of a fatty acid alkyl ester alkoxylate is sufficiently reduced. When the C/B ratio is 0.9 or more, in the production process of a fatty acid alkyl ester alkoxylate, the distribution of the addition mole number of the alkylene oxide in the fatty acid alkyl ester alkoxylate is likely to be widened. In order to widen the addition mole number of the alkylene oxide, it is preferable that the C/B ratio be 0.93 or more.

10 When the C/B ratio is no more than the upper limit of the above-mentioned range, the activity of the obtainable catalyst can be enhanced, and therefore, a fatty acid alkyl ester alkoxylate can be produced efficiently. When the C/B ratio is less than 1, the activity of the catalyst can be enhanced prominently.

In the step, the weight ratio represented by [the component (B) + the component
15 (C)]/the component (A) (hereinafter, sometimes referred to as “(B+C)/A ratio”) is preferably 1 to 1/3, more preferably 1 to 1/2.5. When the weight ratio is no more than the upper limit of the above-mentioned range, these components can be stirred easily, and therefore, the component (B) and the component (C) can be mixed efficiently. When the weight ratio is less than the lower limit of the above-mentioned range, the amount of
20 the active component of the catalyst in the component (A) is reduced, and therefore, in the production of a fatty acid alkyl ester alkoxylate, the addition amount of the alkoxylation catalyst becomes too large, which is insufficient.

[0036]

In the step, the temperature condition (i.e., reaction temperature) is preferably 10
25 to 60°C, and more preferably 20 to 50°C. When the temperature is less than the lower

limit of the above-mentioned range, the reaction speed of the component (B) and the component (C) becomes too slow, and hence, the production efficiency of the alkoxylation catalyst is likely to be deteriorated. When the temperature is greater than the upper limit of the above-mentioned range, the activity of the obtainable alkoxylation catalyst is likely to be deteriorated.

The temperature control of the inner of the stirring tank is conducted by flowing a heating medium (e.g., water) having an arbitrary temperature in the jacket.

[0037]

In the step, the stirring time (i.e., reaction time) is the time required to react the component (B) and the component (C) sufficiently and to control heat generation caused by addition of the component (C). For example, the stirring time is preferably 1 to 2 hours.

[0038]

After the mixing step, a catalyst aging in which the alkoxylation catalyst is stirred at an arbitrary temperature may be employed. The temperature condition in the catalyst aging process is preferably 10 to 60°C, and more preferably 20 to 50°C. By employing the step, the amount of unreacted component (B) can be reduced.

In the step, the stirring time is preferably 0.5 to 3 hours.

[0039]

Furthermore, by filtration or settled separation of the alkoxylation catalyst, the concentration of the active component in the alkoxylation catalyst may be enhanced.

[0040]

(Method for producing fatty acid alkyl ester alkoxylate)

The method for producing a fatty acid alkyl ester alkoxylate of the present invention is a method including: adding an alkylene oxide to a fatty acid alkyl ester

represented by general formula (I) shown below (hereafter, sometimes referred to as “component (α)”) in the presence of an alkoxylation catalyst of the present invention.

[0041]



5 [In the formula (I), R^{11} is a hydrocarbon group having 1 to 40 carbon atoms; and R^{12} is a linear alkyl group having 1 to 3 carbon atoms.]

[0042]

In the formula (I), the number of carbon atoms of R^{11} is 1 to 40, preferably 3 to 30, and more preferably 5 to 21.

10 R^{11} may be linear or branched.

R^{11} may be a saturated hydrocarbon group (alkyl group) or an unsaturated hydrocarbon group such as an alkenyl group.

[0043]

In the aforementioned formula (I), R^{12} is preferably a linear alkyl group having 1
15 to 3 carbon atoms, and more preferably a methyl group having one carbon atom.

[0044]

Examples of the component (α) include a fatty acid methyl ester such as methyl decanoate, methyl laurate, methyl myristate, and methyl oleate, and a mixture thereof.

The component (α) may be the same as the fatty acid alkyl ester used as the
20 component (A), or may be different from each other.

[0045]

The alkylene oxide is selected according to the objective product. For example, in order to obtain a non-ionic surfactant, ethylene oxide, propylene oxide, butylene oxide and the like are preferably used, and ethylene oxide and propylene oxide are more
25 preferably used. As the alkylene oxide, one type may be used, or two or more types

may be used in combination.

[0046]

Hereafter, an example of the method for producing a fatty acid alkyl ester alkoxyate of the present invention will be explained below.

5 The method for producing a fatty acid alkyl ester alkoxyate of this embodiment is a method including: adding an alkylene oxide to the component (α) in the presence of an alkoxylation catalyst of the present invention, and the method includes a catalyst dispersing step, an addition reaction step, and a maturing step.

[0047]

10 The catalyst dispersing step is a step in which the alkoxylation catalyst is dispersed into the component (α) as a starting material. In the step, by using a reactor equipped with a mixing tank having a jacket and a paddle stirring blade provided in the stirring tank, and the component (α) and the alkoxylation catalyst are stirred in the stirring tank.

15 For example, the weight ratio represented by the component (α)/the alkoxylation catalyst (hereafter, sometimes referred to as “raw material/catalyst ratio”) is preferably 20 to 1,000, and more preferably 30 to 200. The raw material/catalyst ratio may be appropriately determined taking into consideration the objective reaction time. When
20 the raw material/catalyst ratio is too small, the separation of the catalyst after the reaction is complicated.

[0048]

 In the step, the temperature condition is not particularly limited, and for example, room temperature (e.g., 5 to 35°C) can be applied. The temperature control in the stirring tank is conducted by flowing a heating medium (e.g., water) having an arbitrary
25 temperature in the jacket.

In the step, the stirring time is not particularly limited, and is the time required to disperse the component (α) into the alkoxylation catalyst to be a substantially uniform dispersion.

[0049]

5 The addition reaction step is a step in which an alkylene oxide is added to the component (α) to obtain a fatty acid alkyl ester alkoxylate.

The step is conducted by allowing the mixture of component (α) and alkoxylation catalyst to come into contact with an alkylene oxide at an arbitrary temperature.

10 In the step, the introduction amount of the alkylene oxide relative to the amount of the component (α) is appropriately determined, taking into consideration the addition mole number of the alkylene oxide in the objective product. For example, the introduction amount is preferably 1 to 100 times the amount of the component (α), preferably 5 to 80 times, and more preferably 10 to 50 times. The production amount of
15 the high-molecular polyethylene glycol becomes large, as the addition mole number becomes larger, that is, as the introduction amount of an alkylene oxide becomes larger. For this reason, the present invention exerts a significant effect in the production of a fatty acid alkyl ester alkoxylate having a large addition mole number.

[0050]

20 In the step, the temperature condition (i.e., addition reaction temperature) is preferably 160 to 180°C.

In the step, the pressure condition is appropriately determined, taking into consideration the addition reaction temperature. For example, 0.1 to 1 MPa is preferable, and 0.1 to 0.6 MPa is more preferable.

25 [0051]

The maturing step is a step in which the inner of the reactor is stirred at an arbitrary temperature after the addition reaction step. By employing the step, the amount of unreacted component (α) can be reduced.

5 In the step, the temperature condition is the same as that of the addition reaction temperature.

[0052]

If necessary, the active component of the catalyst remaining in the fatty acid alkyl ester alkoxylate may be removed. As a method for removing the active component of the catalyst, for example, filtration may be employed. Alternatively, the
10 active component of the catalyst remaining in the fatty acid alkyl ester alkoxylate may not be removed.

[0053]

In this embodiment, the addition reaction step may be conducted in the presence of the alkoxylation catalyst of the present invention and a polyhydric alcohol (hereafter,
15 sometimes referred to as “component (β)”). By conducting the addition reaction step in the presence of the component (β), the amount of production of by-product can be further reduced.

[0054]

Examples of the component (β) include an alkylene glycol such as ethylene
20 glycol, propylene glycol and the like; a polyalkylene glycol such as polyethylene glycol, polypropylene glycol and the like; glycerin and the like. As the component (β), a polyhydric alcohol having a molecular weight of 200 or less is preferable, and an alkylene glycol, a polyalkylene glycol having a molecular weight of 200 or less, and glycerin are more preferable, and ethylene glycol, diethylene glycol, triethylene glycol,
25 tetraethylene glycol and glycerin are still more preferable.

[0055]

The component (β) may coexist with the alkoxylation catalyst in the addition reaction step. The component (β) may be added to the component (α) in the catalyst dispersing step, or may be added to the mixture of the component (α) and the alkoxylation catalyst in the addition reaction step. Alternatively, the component (β) may be mixed with the alkoxylation catalyst in advance.

[0056]

In the addition reaction step, the weight ratio represented by the component (β)/the component (α) is preferably 0.0005 to 0.02, and more preferably 0.001 to 0.01.

When the weight ratio is less than the lower limit of the above-mentioned range, the effect obtainable by addition of the component (β) is less likely to be achieved. When the weight ratio is greater than the upper limit of the above-mentioned range, there is a case where the distribution of the addition mole number of the alkylene oxide becomes too narrow.

[0057]

According to the alkoxylation catalyst of the present invention, since the catalyst is obtainable by reacting the component (B) and the component (C) in the component (A) in a specific C/B ratio, the amount of by-product generated in the production of alkylene oxide adducts can be reduced.

The reasons why the effects of the present invention can be achieved have not been elucidated yet. However, as one reason, it is presumed that by ensuring the specific range of the C/B ratio, the crystal structure of the alkoxylation catalyst becomes a suitable form to suppress the generation of by-products.

EXAMPLES

[0058]

A description of examples of the present invention follows, although the scope of the present invention is in no way limited by these examples.

[0059]

5 (Raw material to be used)

<Component (A)>

- 2-Ethylhexanol: first class grade chemicals, manufactured by Kanto Chemical Co., Inc.

- 2-Propanol: special class grade chemicals, manufactured by Kanto Chemical
10 Co., Inc.

- 1-Hexanol: special class grade chemicals, manufactured by Kanto Chemical Co., Inc.

- 1-Dodecanol: special class grade chemicals, manufactured by Kanto Chemical Co., Inc.

15 - Methyl laurate: pastel M12, manufactured by Lion Chemical Co., Ltd.

[0060]

<Component (B)>

- Calcium acetate monohydrate: special class grade chemicals, manufactured by Kanto Chemical Co., Inc.

20 - Calcium oxide: manufactured by Wako Pure Chemical Industries, Ltd.

<Component (B'): Comparative component of component (B) >

- Potassium acetate: special class grade chemicals, manufactured by Kanto Chemical Co., Inc.

- Calcium carbonate: special class grade chemicals, manufactured by Kanto
25 Chemical Co., Inc.

- Calcium sulfate dihydrate: first class grade chemicals, manufactured by Kanto Chemical Co., Inc.

- Calcium sulfate hemihydrate: first class grade chemicals, manufactured by Kanto Chemical Co., Inc.

5 [0061]

<Component (C)>

- Sulphuric acid: special class grade chemicals, concentration: 96% by weight, manufactured by Kanto Chemical Co., Inc.

<Component (C'): Comparative component of component (C)>

10 - Phosphoric acid: special class grade chemicals, concentration: 85% by weight, manufactured by Kanto Chemical Co., Inc.

[0062]

<Component (β)>

15 - Ethylene glycol: special class grade chemicals, manufactured by Kanto Chemical Co., Inc.

- Diethylene glycol: special class grade chemicals, manufactured by Kanto Chemical Co., Inc.

- Glycerin: special class grade chemicals, manufactured by Kanto Chemical Co., Inc.

20 [0063]

(Examples 1-1 to 1-7, Comparative Examples 1-1 to 1-5, 1-7 and 1-8)

In accordance with the catalyst composition indicated in Tables 1 and 2, a component (B) or component (B') and a component (A) were added to a beaker of 500 mL, followed by mixing at room temperature (i.e., 25°C) using a paddle stirring blade, 25 thereby obtaining a dispersed material (dispersing step). While stirring the dispersed

material, a component (C) or component (C') was added thereto over 10 minutes using a dropping funnel to mix these components (mixing step). In the mixing step, heat was generated by addition of sulphuric acid, and hence, the beaker was cooled in a water bath to control the reaction temperature within 30 to 50°C. After addition of the component (C) or component (C'), stirring was further conducted for 2 hours while maintaining the temperature at 50 °C (maturing step), thereby obtaining an alkoxylation catalyst in each of examples.

The amount of each component indicated in the Tables is a corresponding value expressed in terms of pure content (the same applies below).

10 [0064]

12.5 g of the alkoxylation catalyst obtained in each of examples, 462 g of methyl laurate (product name: pastel M12, manufactured by Lion Chemical Co., Ltd.), and 166 g of methyl myristate (product name: pastel M14, manufactured by Lion Chemical Co., Ltd.) were fed in an autoclave, followed by stirring (catalyst dispersing step). While stirring, the autoclave was purged with nitrogen. The temperature was raised to 100°C. Dehydration was conducted under a vacuum condition at 1.3 kPa or less for 30 minutes. Next, the temperature was raised to the addition reaction temperature indicated in Tables, introduction of 1,876 g of ethylene oxide (EO) (15 times the sum of methyl laurate and methyl myristate) was conducted, followed by stirring for the addition reaction time indicated in Tables (addition reaction step). Then, after stirring at the addition reaction temperature for 0.5 hour (maturing step), the reaction mixture was cooled to 80°C, thereby obtaining 2,516 g of crude reaction product (fatty acid methyl ester ethoxylate (MEE), average addition mole number of EO = 15). The amount of high-molecular polyethylene glycol (high-molecular PEG) in the crude reaction product was determined in accordance with a gel permeation chromatography (GPC) method. The results are

25

shown in Tables. The condition for determination described later was employed in GPC method.

With respect to Comparative Examples 1-1 to 1-3 and Comparative Examples of 1-5, 1-7 and 1-8, even though the addition reaction time was extended to 24 hours, MEE
5 was not produced, and therefore, determination of the amount of high-molecular PEG was not conducted.

[0065]

<Condition for determination in accordance with GPC method>

- Column: Shodex Asahipak GF-310HQ, manufactured by Showa Denko K.K.
- 10 - Detector: Differential refractive index detector RID-10A, manufactured by Shimadzu Corporation

[0066]

(Comparative Example 1-6)

Alumina·Magnesium hydroxide represented by $2.5\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$
15 (Kyoward300, manufactured by Kyowa Chemical Industry Co., Ltd.) was calcined at 900°C for 3 hours, thereby obtaining Magnesium·Aluminum composite metal oxide catalyst.

[0067]

2.5 g of the composite metal oxide catalyst, 462 g of methyl laurate, 166 g of
20 methyl myristate, and 3 g of glycerin were fed in an autoclave, and then 1.3 g of 10% by weight of potassium hydroxide was added thereto, followed by stirring for 10 minutes (alkali modification treatment of composite metal oxide catalyst).

Then, while stirring, the autoclave was purged with nitrogen. The temperature was raised to 100°C. Dehydration was conducted under a vacuum condition at 1.3 kPa
25 or less for 30 minutes.

Next, introduction of 1,876 g of ethylene oxide (EO) was conducted at an addition reaction temperature of 180°C and at a pressure of 0.5MPa, followed by stirring for 7 hours (addition reaction step). Then, after stirring at a temperature of 180°C for 0.5 hour (maturing step), the reaction mixture was cooled to 80°C, thereby obtaining 5 2,506 g of crude reaction product (MEE, average addition mole number of EO = 15). The amount of high-molecular PEG in the crude reaction product was determined in accordance with a GPC method. The results are shown in Tables.

[0068]

[Table 1]

			Example						
			1-1	1-2	1-3	1-4	1-5	1-6	1-7
Catalyst composition	Component (A)	2-ethylhexanol (g)	137	137	137	-	-	-	-
		2-propanol (g)	-	-	-	137	-	-	-
		1-hexanol (g)	-	-	-	-	137	-	-
		1-dodecanol (g)	-	-	-	-	-	137	
		Methyl laurate (g)	-	-	-	-	-	-	137
	Component (B)	Calcium acetate monohydrate (g)	41.7	41.7	41.7	41.7	41.7	41.7	41.7
	Component (B')	Potassium acetate (g)	-	-	-	-	-	-	-
		Calcium carbonate (g)	-	-	-	-	-	-	-
		Calcium acetate dihydrate (g)	-	-	-	-	-	-	-
		Calcium acetate hemihydrate (g)	-	-	-	-	-	-	-
	Component (C)	Sulphuric acid	20.9	18.6	23.2	20.9	20.9	20.9	20.9
	Component (C')	Phosphoric acid	-	-	-	-	-	-	-
	Modified catalyst (% by weight)		-	-	-	-	-	-	-
	C/B ratio		0.9	0.8	0.96	0.9	0.9	0.9	0.9
	(B+C)/A ratio		0.46	0.44	0.47	0.46	0.46	0.46	0.46
Condition for production of MEE	Introduction amount of EO (mole number per 1 mole of fatty acid ester)		15	15	15	15	15	15	15
	Addition reaction temperature (°C)		160	160	160	160	160	170	160
	Addition reaction time (hours)		6.5	7.0	6.5	6.5	6.5	7.0	6.5
Result	Amount of high-molecular PEG (% by weight)		0.10	0.10	0.06	0.15	0.10	0.08	0.15

[0069]

[Table 2]

			Comparative Example							
			1-1	1-2	1-3	1-4	1-5	1-6	1-7	1-8
Catalyst composition	Component (A)	2-ethylhexanol (g)	137	137	137	137	137	-	137	137
		2-propanol (g)	-	-	-	-	-	-	-	-
		1-hexanol (g)	-	-	-	-	-	-	-	-
		1-dodecanol (g)	-	-	-	-	-	-	-	-
		Methyl laurate (g)	-	-	-	-	-	-	-	-
	Component (B)	Calcium acetate monohydrate (g)	-	-	41.7	41.7	41.7	-	-	-
	Component (B')	Potassium acetate (g)	42.1	-	-	-	-	-	-	-
		Calcium carbonate (g)	-	34.0	-	-	-	-	-	-
		Calcium acetate dihydrate (g)	-	-	-	-	-	-	40.8	-
		Calcium acetate hemihydrate (g)	-	-	-	-	-	-	-	34.4
	Component (C)	Sulphuric acid	18.9	30.0	-	10.4	27.9	-	-	-
	Component (C')	Phosphoric acid	-	-	20.9	-	-	-	-	-
	Modified catalyst (% by weight)		-	-	-	-	-	100	-	-
	C/B ratio		0.45	0.9	0.9	0.45	1.2	-	-	-
	(B+C)/A ratio		0.45	0.47	0.46	0.38	0.51	-	-	-
Condition for production of MEE	Introduction amount of EO (mole number per 1 mole of fatty acid ester)		15	15	15	15	15	15	0.5	0.5
	Addition reaction temperature (°C)		160	160	160	160	160	180	160	160
	Addition reaction time (hours)		-	-	-	21	-	7	-	-
Result	Amount of high-molecular PEG (% by weight)		-	-	-	0.53	-	1.0	-	-

[0070]

As shown in Table 1, the amount of high-molecular PEG in Examples 1-1 to 1-7 of the present invention was 0.15% by weight or less.

On the other hand, as shown in Table 2, in Comparative Examples 1-1, 1-2, 1-7
5 and 1-8 in which the component (B') was used instead of the component (B), Comparative Example 1-3 in which the component (C') was used instead of the component (C), and Comparative Example 1-5 in which the C/B ratio was 1.2, MEE could not be produced.

In Comparative Example 1-4 in which the C/B ratio was 0.45, the amount of
10 high-molecular PEG was 0.53% by weight. In Comparative Example 1-6 in which the composite metal oxide catalyst was used, the amount of high-molecular PEG was 1.0% by weight.

From the results, it was confirmed that, by applying the present invention, MEE could be produced while reducing the production amount of high-molecular PEG.

15 [0071]

(Examples 2-1 to 2-9, Comparative Examples 2-1 to 2-3)

In accordance with Tables 3 and 4, the component (A) and the component (B) were added to a separable flask of 1,000 mL, followed by mixing at room temperature (25°C) using a dispersion-type stirring blade thereby obtaining a dispersed material
20 (dispersing step). While stirring the dispersed material, the component (C) was added thereto over 60 minutes using a dropping funnel to mix these components (mixing step). In the mixing step, heat was generated by addition of sulphuric acid, and hence, the flask was cooled in a water bath to control the reaction temperature of 20 to 40°C. After addition of the component (C), stirring was further conducted for 2 hours while
25 maintaining the temperature at 25 °C (catalyst maturing step), thereby obtaining an

alkoxylation catalyst in each of examples.

[0072]

In accordance with “Condition for production of MEE”, MEE was produced in the following manner.

5 The alkoxylation catalyst obtained in each of examples, the component (β), methyl laurate (product name: pastel M12, manufactured by Lion Chemical Co., Ltd.), and methyl myristate (product name: pastel M14, manufactured by Lion Chemical Co., Ltd.) were fed into an autoclave, followed by stirring (catalyst dispersing step). Then, under a condition at 0.1 to 0.5 kPa and at the addition reaction temperature indicated in
10 Tables, introduction of ethylene oxide (EO) was conducted, followed by stirring for the addition reaction time indicated in Tables (addition reaction step). Then, after stirring at the addition reaction temperature for 0.5 hour (maturing step), the reaction mixture was cooled to 80°C, thereby obtaining a crude reaction product (MEE, average addition mole number of EO = 15). The amount of high-molecular PEG in the crude reaction product
15 was determined by a GPC method. The results are shown in Tables.

The distribution of the addition mole number of EO in the crude reaction product (addition mole distribution of EO) was determined in accordance with a gas chromatography (GC) method. These results are shown in Tables. The condition for determination described later was employed in GC. The addition mole distribution of
20 EO (GC area %) is calculated in accordance with the following calculation method. The distribution of the addition mole number of EO becomes wider as the value of the addition mole distribution of EO is smaller.

With respect to Comparative Example 2-2, even though the addition reaction time was extended to 24 hours, MEE was not produced, and therefore, determination of
25 the amount of high-molecular PEG was not conducted.

[0073]

<Condition for determination in accordance with GC method>

- Gas chromatograph: GC-2025, manufactured by Shimadzu Corporation

- Column: DB-1 HT, length: 30 m, inner diameter: 0.25 mm, film thickness: 0.1

5 μm, manufactured by Agilent Technologies, Inc.

- Mobile phase: helium

- Detector: Flame ionization detector (FID), 380°C

- Inlet: Split, 380°C

- Temperature: from 100°C to 380°C

10 - Based on the peak area, the addition mole distribution of EO was calculated in accordance with the following equation.

[0074]

<Calculation method>

The addition mole distribution of EO was calculated by the following equation.

15 {(area of maximum peak (P1) detected as methyl laurate) + (sum of area of two peaks around the maximum peak P1) + (area of maximum peak (P2) detected as methyl myristate) + (sum of area of two peaks around the maximum peak P2)} ÷ total peak area

[0075]

[Table 3]

			Example					
			2-1	2-2	2-3	2-4	2-5	2-6
Catalyst composition	Component (A)	Methyl laurate (g)	525	525	525	-	-	525
		2-ethylhexanol (g)	-	-	-	525	525	-
	Component (B)	Calcium acetate monohydrate (g)	150	150	150	150	150	150
		Calcium oxide (g)	-	-	-	-	-	-
	Component (C)	Sulphuric acid (g)	72.2	76.0	80.2	72.2	76.0	72.2
	C/B ratio		0.86	0.91	0.96	0.86	0.91	0.86
	(B+C)/A ratio		0.42	0.43	0.44	0.42	0.43	0.42
Condition for production of MEE	Introduction amount of EO (mole number per 1 mole of fatty acid ester)		12.5	12.5	12.5	12.5	12.5	12.5
	Introduction amount of EO (g)		1875	1875	1875	1875	1875	1875
	Component (α)	Methyl laurate (g)	472	472	472	472	472	472
		Methyl myristate (g)	169	169	169	169	169	169
	Mixture of catalyst (g)		12.5	12.5	12.5	12.5	12.5	12.5
	Component (β)	Ethylene glycol (g)	-	-	-	-	-	1.6
		Diethylene glycol (g)	-	-	-	-	-	-
		Glycerin (g)	-	-	-	-	-	-
	Addition reaction temperature (°C)		160	160	160	160	160	160
	Addition reaction time (hours)		6.5	6.0	6.0	6.5	6.0	5.5
Result	Amount of high-molecular PEG (% by weight)		0.15	0.08	0.09	0.10	0.10	0.05
	Distribution of addition mole number of EO (GC area %)		55.4	53.1	43.7	56.8	55.1	55.7

[0076]

[Table 4]

			Example			Comparative Example		
			2-7	2-8	2-9	2-1	2-2	2-3
Catalyst composition	Component (A)	Methyl laurate (g)	525	525	-	525	525	-
		2-Ethylhexanol (g)	-	-	420	-	-	420
	Component (B)	Calcium acetate monohydrate (g)	150	150	-	150	150	-
		Calcium oxide (g)	-	-	120	-	-	120
	Component (C)	Sulphuric acid (g)	76.0	72.2	181.3	56.16	83.3	91.5
	C/B ratio		0.91	0.86	0.86	0.67	1.1	0.4
	(B+C)/A ratio		0.43	0.42	0.72	0.39	0.45	0.50
Condition for production of MEE	Introduction amount of EO (mole number per 1 mole of fatty acid ester)		12.5	12.5	15	12.5	12.5	15
	Introduction amount of EO (g)		1875	1875	1875	1875	1875	1875
	Component (α)	Methyl laurate (g)	472	472	472	472	472	472
		Methyl myristate (g)	169	169	169	169	169	169
	Mixture of catalyst		12.5	12.5	15	12.5	12.5	15
	Component (β)	Ethylene glycol (g)	-	-	-	-	-	-
		Diethylene glycol (g)	1.5	-	2.7	-	-	2.7
		Glycerin (g)	-	1.2	-	-	-	-
	Addition reaction temperature (°C)		160	160	180	160	160	180
	Addition reaction time (hours)		5.5	6.0	6.5	7.0	-	7.0
Result	Amount of high-molecular PEG (% by weight)		0.03	0.08	0.22	0.40	-	0.42
	Distribution of addition mole number of EO (GC area %)		53.6	48.6	39.8	57.0	-	64.7

[0077]

As shown in Tables 3 and 4, the amount of high-molecular PEG in Examples 2-1 to 2-9 of the present invention was 0.22% by weight or less.

In comparison between Example 2-1 and Examples 2-6 to 2-8, Examples 2-6 to 2-8 in which the addition reaction step was conducted in the presence of the component (β), reaction speed could be enhanced, and the amount of high-molecular PEG could be reduced as compared to Example 2-1 in which the component (β) was not used.

In comparison of Examples 2-1 to 2-3, the distribution of the addition mole number of EO became wider as the C/B ratio was enhanced.

In contrast, the amount of high-molecular PEG in Comparative Examples 2-1 to 2-3 in which the C/B ratio was less than 0.8 was 0.40% by weight or more.

From the results, it was confirmed that, by applying the present invention, MEE could be produced while reducing the amount of production of high-molecular PEG prominently.

INDUSTRIAL APPLICABILITY

[0078]

The catalyst according to the present invention can suppress the generation of by-products in the production of a fatty acid alkyl ester alkoxylate. For this reason, the fatty acid alkyl ester alkoxylate produced by using the alkoxylation catalyst of the present invention is useful as a non-ionic surfactant for a liquid detergent.

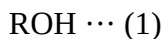
CLAIMS

1. An alkoxylation catalyst for use in a reaction of alkoxylation of a fatty acid alkyl ester represented by general formula (I) shown below, the alkoxylation catalyst being
 5 formed when a component (B) that is at least one member selected from the group consisting of an alkaline-earth metal salt of a carboxylic acid, an alkaline-earth metal salt of a hydroxycarboxylic acid, an oxide of an alkaline-earth metal and a hydroxide of an alkaline-earth metal and a component (C) that is sulphuric acid are reacted in a component (A) that is a liquid dispersion medium, wherein the molar ratio represented by
 10 the component (C)/the component (B) is 0.8 to 1:



in the formula (I), R^{11} is a hydrocarbon group having 1 to 40 carbon atoms; and R^{12} is a linear alkyl group having 1 to 3 carbon atoms.

15 2. The alkoxylation catalyst according to Claim 1, wherein the component (A) is at least one member selected from the group consisting of an alcohol represented by general formula (1) shown below, an alkylene oxide adduct of the alcohol, a fatty acid alkyl ester represented by general formula (2) shown below, an alkylene oxide adduct of the fatty acid alkyl ester, a fatty acid represented by general
 20 formula (3) shown below and an alkylene oxide adduct of the fatty acid:



in the formula (1), R is a hydrocarbon group having 3 to 18 carbon atoms;



in the formula (2), R^1 is a hydrocarbon group having 3 to 18 carbon atoms; and

25 R^2 is a linear alkyl group having 1 to 3 carbon atoms; and



in the formula (3), R^3 is a hydrocarbon group having 3 to 18 carbon atoms.

3. A method for producing an alkoxylation catalyst, comprising:

5 mixing a component (B) that is at least one member selected from the group consisting of an alkaline-earth metal salt of a carboxylic acid, an alkaline-earth metal salt of a hydroxycarboxylic acid, an oxide of an alkaline-earth metal and a hydroxide of an alkaline-earth metal and a component (C) that is sulphuric acid are reacted in a component (A) that is a liquid dispersion medium, wherein

10 the molar ratio represented by the component (C)/the component (B) is 0.8 to 1.

4. The method for producing an alkoxylation catalyst according to Claim 3, wherein

the weight ratio represented by [the component (B) + the component (C)]/the
15 component (A) is 1 to 1/3.

5. A method for producing a fatty acid alkyl ester alkoxylate, comprising
adding an alkylene oxide to a fatty acid alkyl ester in the presence of an
alkoxylation catalyst of Claim 1 or 2.

20

6. A method for producing a fatty acid alkyl ester alkoxylate, comprising
adding an alkylene oxide to a fatty acid alkyl ester in the presence of a
polyhydric alcohol and an alkoxylation catalyst of Claim 1 or 2.

25