

[DESCRIPTION]

[TITLE OF INVENTION]

METHOD FOR PRODUCING FATTY ACID AKLYL ESTER ALKOXYLATE

5

[Technical Field]

[0001]

The present invention relates to a method for producing a fatty acid alkyl ester alkoxylate.

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Priority is claimed on Japanese Patent Application No. 2014-090579, filed April 24, 2014, the content of which is incorporated herein by reference.

[Background Art]

[0002]

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Fatty acid alkyl ester alkoxylates in which alkylene oxides are added to fatty acid alkyl esters have been widely used as cleaning components of liquid detergents.

Fatty acid alkyl ester alkoxylates are used as nonionic surfactants in detergents for clothing or the like. Fatty acid alkyl ester alkoxylates have been utilized as particularly suitable for concentrated liquid detergents in which surfactants are incorporated in high concentrations, since the gelling area is small even when incorporated in high concentrations (see Patent Document 1).

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Examples of the method for producing fatty acid alkyl ester alkoxylates include a method of adding an alkylene oxide to a fatty acid alkyl ester in the presence of an alkoxylation catalyst.

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[0003]

In general, for the alkoxylation reaction of alcohols, amines and the like that have an active hydrogen such as hydrogen in a hydroxyl group in the molecule, homogeneous catalysts such as acids and alkalis and/or heterogeneous catalysts such as composite metal oxides have been used as alkoxylation catalysts. However, an addition
5 reaction of alkylene oxide to fatty acid alkyl esters having no active hydrogen in the molecule (also referred to as an alkoxylation reaction) does not proceed with an acid catalyst or an alkali catalyst such as sodium hydroxide which is a homogeneous catalyst. For this reason, in the above alkoxylation reaction, a composite metal oxide catalyst or the like is used. Examples of the composite metal oxide catalyst include
10 aluminum/magnesium-based composite metal oxides such as calcined products of aluminum magnesium hydroxide and the like (see Patent Document 2).

When performing an alkoxylation reaction of fatty acid alkyl esters using a composite metal oxide catalyst such as the aforementioned aluminum/magnesium-based composite metal oxide, a step for removing the catalyst such as filtration is required after
15 the reaction. Further, when a composite metal oxide catalyst such as the aforementioned aluminum/magnesium-based composite metal oxide is used, polymer by-products (molecules having a weight average molecular weight of 10,000 or more as measured by the gel permeation chromatography method) such as polyalkylene glycols are produced during the reaction, and there is a problem that when a fatty acid alkyl ester
20 alkoxyate containing such by-products is used in a liquid detergent, the liquid detergent easily becomes cloudy. Therefore, it becomes necessary to also remove these types of byproducts such as polyalkylene glycol having a high molecular weight together with the catalyst. However, these polyalkylene glycols and the like having a high molecular weight are likely to cause clogging of filter cloth, and the filtration rate is reduced as a
25 result. Therefore, a large filtration system will be required from an industrial

perspective, and there is a problem that the system burden on business operators increases.

Accordingly, in the alkoxylation reaction of fatty acid alkyl esters, as a catalyst for reducing the produced amount of such by-products, an alkoxylation catalyst obtained
5 by reacting at least one alkaline earth metal compound selected from the group consisting of alkaline earth metal salts of carboxylic acids, alkaline earth metal salts of hydroxycarboxylic acids, oxides of alkaline earth metals and hydroxides of alkaline earth metals with sulfuric acid in a liquid dispersion medium, and in which a molar ratio represented by the formula (acid)/(alkaline earth metal compound) is from 0.8 to 1, has
10 been proposed (see Patent Document 3). Hereinafter, this type of catalyst obtained by reacting an alkaline earth metal compound and acid in a liquid dispersion medium will be referred to as an acid/alkaline earth metal compound catalyst.

[Prior Art Document]

15 [Patent Documents]

[0004]

[Patent Document 1] International Publication No. WO 2011/007778

[Patent Document 2] International Publication No. WO 2008/078768

[Patent Document 3] International Publication No. WO 2013/154189

20 [Patent Document 4] International Publication No. WO 2008/001797

[Disclosure of Invention]

[Problems to be solved by the Invention]

[0005]

25 However, as a result of intensive studies conducted by the inventors of the

present invention, when a fatty acid alkyl ester alkoxylate obtained by using an acid/alkaline earth metal compound catalyst described in Patent Document 3 is used in a liquid detergent, it was found that there is a problem that the liquid detergent tends to solidify at a low temperature condition of less than 0°C. It is desirable to keep the liquid detergent in a liquid form without causing solidification, precipitation, or the like at low temperatures in order to be used or stored in cold regions. For this reason, for example, the blending composition is arranged so as to maintain the liquid form in a storage test of one month at -5°C.

Here, the distribution of the number of moles of ethylene oxide added to the fatty acid alkyl ester alkoxylate to be used in the liquid detergent has been known to affect the viscosity of the liquid detergent (Patent Document 4).

On the other hand, according to studies conducted by the inventors of the present invention, a problem that a liquid detergent is likely to solidify in low temperature conditions of below 0°C does not occur when a fatty acid alkyl ester alkoxylate produced using the aforementioned composite metal oxide catalyst is used for the production of the liquid detergent (see Comparative Examples in the present application). However, as mentioned earlier, in the case of using a composite metal oxide catalyst, there is a problem of burden to filter the catalyst and by-products.

The present invention takes the above circumstances into consideration, with an object of providing a method for producing a fatty acid alkyl ester alkoxylate useful as a cleaning component of a liquid detergent that is less likely to solidify at a low temperature condition of less than 0°C, which is also a method that produces a fatty acid alkyl ester alkoxylate using the aforementioned acid/alkaline earth metal compound catalyst in order to reduce the production of the aforementioned by-products in producing the fatty acid alkyl ester alkoxylate.

[Means for Solving the Problems]

[0006]

As a result of intensive investigation, the inventors of the present invention propose the following aspects in order to achieve the object described above.

5 That is, the method for producing a fatty acid alkyl ester alkoxylate according to the present invention is a method for producing a fatty acid alkyl ester alkoxylate by adding an alkylene oxide to a fatty acid alkyl ester represented by the following general formula (I), the method characterized by including a step of adding 5 to 25 moles of the
10 aforementioned alkylene oxide relative to 1 mole of the aforementioned fatty acid alkyl ester in the presence of an alkoxylation catalyst obtained by reacting an alkaline earth metal compound (B) and at least one acid (C) selected from the group consisting of sulfuric acid, hydrochloric acid and phosphoric acid in a liquid dispersion medium (A), and 0.05 to 0.20 moles of at least one alcohol selected from a group consisting of a monohydric alcohol and a dihydric alcohol (hereinafter, also referred to as a
15 monovalent/divalent alcohol) with respect to 1 kg of the aforementioned fatty acid alkyl ester, and wherein the molar ratio of the aforementioned acid (C) to the aforementioned alkaline earth metal compound (B) (C/B ratio) is equal to or more than 0.8 but less than 1.



[In the formula (I), R^{11} is a hydrocarbon group of 7 to 17 carbon atoms, and R^{12}
20 is a linear alkyl group of 1 to 3 carbon atoms.]

It should be noted that the amount of the fatty acid alkyl ester, monohydric/dihydric alcohol and alkylene oxide used can be adjusted by a production facility, and the like, and is not limited as long as it satisfies the above-mentioned ratio.

Further, one aspect of the present invention is a method for producing a fatty
25 acid alkyl ester alkoxylate, including

a catalyst production step of producing an alkoxylation catalyst by reacting the alkaline earth metal compound (B) and at least one acid (C) selected from the group consisting of sulfuric acid, hydrochloric acid and phosphoric acid in the liquid dispersion medium (A);

5 a catalyst dispersion step of mixing the aforementioned catalyst and the aforementioned fatty acid alkyl ester represented by the general formula (I);

an addition reaction step of further adding from 5 to 25 moles of alkylene oxide, with respect to 1 mole of the aforementioned fatty acid alkyl ester, to the reaction solution obtained in the catalyst dispersion step; and

10 mixing 0.05 to 0.20 moles of the monohydric/dihydric alcohol, relative to 1 kg of the fatty acid alkyl ester, with the aforementioned reaction solution before adding the aforementioned additional alkylene oxide.

[Advantageous Effects of Invention]

15 [0007]

According to the method of the present invention for producing a fatty acid alkyl ester alkoxyate, by using a certain amount of monohydric/dihydric alcohol in the reaction system, a fatty acid alkyl ester alkoxyate useful as a cleaning component of a liquid detergent that suppresses solidification in low temperature conditions and exhibits
20 favorable fluidity can be produced.

[Description of Embodiments]

[0008]

(Method for producing fatty acid alkyl ester alkoxyate)

25 A method for producing a fatty acid alkyl ester alkoxyate according to the

present invention includes a step of adding a certain amount of alkylene oxide to the fatty acid alkyl ester represented by the following general formula (I) in the presence of a specific alkoxylation catalyst and a certain amount of monohydric/dihydric alcohol.

[0009]

5 <Fatty acid alkyl ester>



[In the formula (I), R^{11} is a hydrocarbon group of 7 to 17 carbon atoms, and R^{12} is a linear alkyl group of 1 to 3 carbon atoms.]

[0010]

10 In the above formula (I), the lower limit of the number of carbon atoms of R^{11} is 7, preferably 9, and more preferably 11, and the upper limit thereof is 17, preferably 15, and more preferably 13. In the above formula (I), the number of carbon atoms of R^{11} is preferably from 9 to 15, and more preferably from 11 to 13.

R^{11} may be linear or branched. R^{11} is preferably linear.

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

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

20 [0011]

More specifically, as the fatty acid alkyl ester, fatty acid methyl esters, mixtures thereof, or the like are preferred, and methyl laurate, methyl myristate, mixtures thereof, or the like are more preferred.

One type of the fatty acid alkyl ester may be used alone, or two or more types
25 may be used in combination.

[0012]

<Alkylene oxide>

The alkylene oxide is determined in accordance with the target product. For example, in order to obtain a nonionic surfactant, ethylene oxide, propylene oxide, butylene oxide, and the like are preferred, and among these, ethylene oxide is more preferred.

One type of the alkylene oxide may be used alone, or two or more types may be used in combination.

[0013]

10 <Certain amount of monohydric/dihydric alcohol>

At least one alcohol selected from the group consisting of monohydric alcohols and dihydric alcohols to be used in a certain amount (also referred to as a monohydric/dihydric alcohol) may be a saturated alcohol, or may be an unsaturated alcohol.

15 Examples of the monohydric/dihydric alcohol to be used in a certain amount include monohydric alcohols such as methanol, ethanol, propanols such as 2-propanol, butanol, pentanol, hexanol, heptanol, octanols such as n-octanol and 2-ethylhexanol, nonanol, decanol, undecyl alcohol, lauryl alcohol, tridecyl alcohol, myristyl alcohol, pentadecyl alcohol, stearyl alcohol, isostearyl alcohol, and oleyl alcohol; alkylene glycols
20 such as ethylene glycol and propylene glycol; alkoxyalkylene glycol in which one terminal is alkoxyated, and the like.

Among them, the monohydric/dihydric alcohol to be used in a certain amount is preferably a monohydric alcohol, more preferably a linear or branched monohydric alcohol of 1 to 18 carbon atoms, still more preferably a linear or branched monohydric
25 alcohol of 1 to 8 carbon atoms, and particularly preferably 2-propanol or 2-ethylhexanol.

One type of the monohydric/dihydric alcohol to be used in a certain amount may be used alone, or two or more types thereof may be used in combination.

[0014]

<Alkoxylation catalyst>

5 An alkoxylation catalyst in the present invention (hereinafter, also referred to as a “catalyst (α)”) is one obtained by reacting an alkaline earth metal compound (B) (hereinafter, also referred to as a “component (B)”) and at least one acid (C) selected from the group consisting of sulfuric acid, hydrochloric acid and phosphoric acid (hereinafter, also referred to as a “component (C)”) in a liquid dispersion medium (A) (hereinafter, also referred to as a “component (A)”). That is, the aforementioned catalyst (α) contains a reaction product (alkaline earth metal salt which is the main catalytically active component) of the component (B) and the component (C).

One type of the alkoxylation catalyst may be used alone, or two or more types may be used in combination.

15 [0015]

The aforementioned catalyst (α) can be produced by mixing the component (B) and the component (C) in the component (A).

[0016]

- Component (A): liquid dispersion medium

20 The component (A) is not particularly limited as long as it can maintain the fluidity of the reaction solution without being gelled during the preparation of the catalyst (α), and also the component (B) and the component (C) can react in the component (A).

25 The term “liquid” with respect to the component (A) means that it is in a liquid form in the dispersion step and the mixing step described later.

In view of enhancing the productivity in the production method of the catalyst (α) which will be described later, the component (A) is preferably liquid at 30°C.

[0017]

As the component (A), for example, at least one selected from the group
 5 consisting of alcohols represented by the following general formula (1), alkylene oxide adducts of the aforementioned alcohols represented by the formula (1), fatty acid alkyl esters represented by the following general formula (2), alkylene oxide adducts of the aforementioned fatty acid alkyl esters represented by the formula (2), fatty acids represented by the following general formula (3), and alkylene oxide adducts of the
 10 aforementioned fatty acids represented by the formula (3) is preferred.



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



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



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

[0018]

In the above formula (1), for the number of carbon atoms of R, the lower limit
 20 value is 3, and the upper limit value is 18, preferably 12, and more preferably 8. In the above formula (1), the number of carbon atoms of R is preferably at least 3 and not more than 12, and more preferably equal to or more than 3 and equal to or less than 8. If the number of carbon atoms of R is less than the lower limit value, the component (A) is thickened into a gel and loses fluidity during the preparation of the catalyst (α), thereby
 25 making the component (B) and the component (C) difficult to react. If the number of

carbon atoms of R exceeds the upper limit, the melting point becomes high, which makes it unsuitable as the dispersion medium.

R may be linear or branched.

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

Further, the alcohol represented by the above formula (1) is preferably a monohydric alcohol, more preferably a linear or branched monohydric alcohol of 1 to 18 carbon atoms, and still more preferably a linear or branched monohydric alcohol of 1 to 8 carbon atoms. As the alcohol represented by the above formula (1), the same alcohol as the monohydric/dihydric alcohol to be used in a certain amount can be used.

It should be noted that when an alcohol represented by the above formula (1) is used as the component (A), an alcohol derived from the component (A) is included in the monohydric/dihydric alcohol to be used in a certain amount in the production of a fatty acid alkyl ester alkoxylate.

Examples of the alcohol represented by the above formula (1) include primary alcohols such as 1-hexanol, n-octanol, 2-ethylhexanol, n-decanol, n-dodecanol, n-tetradecanol, n-hexadecanol, n-octadecanol, oleyl alcohol, nonanol, undecanol and tridecanol; and secondary alcohols such as 2-propanol, 2-octanol, 2-decanol and 2-dodecanol. Among these, from the viewpoint of further reducing the amount of generated by-products such as high molecular weight polyethylene glycols, 2-propanol and 2-ethylhexanol are preferred.

[0019]

Examples of the alkylene oxide adduct of an alcohol represented by the above formula (1), that is, the alkylene oxide to be added to the alcohol in the alcohol alkoxylate include an alkylene oxide having 2 to 3 carbon atoms.

The average number of moles of alkylene oxide added in the alkylene oxide adduct of an alcohol represented by the above formula (1) is preferably, for example, from 1 to 7.

[0020]

5 In the above formula (2), the number of carbon atoms of R^1 is from 3 to 18, and can be arbitrarily selected as long as the fluidity is satisfactory in the temperature condition during the preparation of the alkoxylation catalyst. In the above formula (2), the number of carbon atoms of R^1 is preferably from 7 to 17, more preferably from 9 to 15, and still more preferably from 11 to 13.

10 R^1 may be linear or branched. R^1 is preferably linear.

R^1 may be a saturated hydrocarbon group, that is, an alkyl group, or may be an unsaturated hydrocarbon group such as an alkenyl group. R^1 is preferably a saturated hydrocarbon group.

15 In the above formula (2), R^2 is a linear alkyl group having 1 to 3 carbon atoms, and preferably a methyl group having one carbon atom. If R^2 is a linear alkyl group having 1 to 3 carbon atoms, the melting point of the component (A) becomes low, and the fluidity becomes satisfactory in a temperature condition at the time of producing the alkoxylation catalyst.

20 As the fatty acid alkyl ester represented by the above formula (2), fatty acid methyl esters such as methyl decanoate, methyl laurate, methyl myristate and methyl oleate, mixtures thereof, or the like are preferred, and methyl laurate, methyl myristate, or a mixture thereof is more preferred. As the fatty acid alkyl ester represented by the above formula (2), since the components other than the target product become even less, it is preferable to use the same fatty acid alkyl ester as the one represented by the general
25 formula (I).

[0021]

Examples of the alkylene oxide adduct of the fatty acid alkyl ester represented by the above formula (2), that is, the alkylene oxide to be added in the fatty acid alkyl ester alkoxylate include an alkylene oxide having 2 to 3 carbon atoms.

5 The average number of moles of alkylene oxide added is preferably, for example, from 1 to 7.

[0022]

In the above formula (3), the number of carbon atoms of R^3 is from 3 to 18, preferably from 7 to 17, and more preferably from 11 to 17. In the above formula (3),
10 the number of carbon atoms of R^3 can be arbitrarily selected as long as the fluidity is satisfactory in the temperature condition during the preparation of the alkoxylation catalyst.

R^3 may be linear or branched.

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

Examples of the fatty acid represented by the above formula (3) include octanoic acid, decanoic acid, lauric acid, palmitoleic acid, oleic acid, linoleic acid and linolenic acid. Among them, oleic acid is preferred.

[0023]

20 Examples of the alkylene oxide to be added in the alkylene oxide adduct of the fatty acid represented by the above formula (3) include an alkylene oxide having 2 to 3 carbon atoms.

The average number of moles of alkylene oxide added is preferably, for example, from 1 to 7.

25 [0024]

As the component (A), from the viewpoint of further reducing the amount of generated by-products, alcohols represented by the general formula (1), and fatty acid alkyl esters represented by the general formula (2) are preferred.

One type of the component (A) may be used alone, or two or more types may be
5 used in combination.

[0025]

- Component (B): alkaline earth metal compound

The component (B) is not particularly limited as long as it is a compound containing an alkaline earth metal and reacts with the component (C).

10 The phrase “alkaline earth metal” with respect to the component (B) includes magnesium and beryllium, in addition to calcium, strontium, barium and radium.

As the component (B), for example, at least one selected from the group consisting of alkaline earth metal salts of carboxylic acids (hereinafter, also referred to as a “component (b1)”), alkaline earth metal salts of hydroxycarboxylic acids (hereinafter, also referred to as a “component (b2)”), oxides of alkaline earth metals (hereinafter, also referred to as a “component (b3)”), hydroxides of alkaline earth metals (hereinafter, also referred to as a “component (b4)”) and alkaline earth metal salts of carbonic acids (hereinafter, also referred to as a “component (b5)”) is preferred.

[0026]

20 Examples of the component (b1) include calcium salts of carboxylic acids such as calcium acetate (anhydrous calcium acetate, calcium acetate monohydrate, and the like) and calcium formate; and barium salts of carboxylic acids such as barium acetate and barium formate. Among these, from the viewpoint of enhancing the catalytic activity, the calcium salts of carboxylic acids are preferred, and calcium acetate is more
25 preferred.

[0027]

Examples of the component (b2) include calcium salts of hydroxycarboxylic acids such as calcium lactate, calcium tartrate, calcium citrate and calcium malate; and barium salts of hydroxycarboxylic acids such as barium lactate, barium tartrate, barium citrate and barium malate. Among these, from the viewpoint of enhancing the catalytic activity, the calcium salts of hydroxycarboxylic acids are preferred.

[0028]

Examples of the component (b3) include calcium oxide and barium oxide, among which calcium oxide is preferred.

10 [0029]

Examples of the component (b4) include calcium hydroxide and barium hydroxide, among which calcium hydroxide is preferred.

[0030]

15 Examples of the component (b5) include calcium carbonate and barium carbonate, among which calcium carbonate is preferred.

[0031]

As the component (B), from the viewpoints of enhancing the catalytic activity and further reducing the amount of generated by-products, the components (b1) and (b3) are preferred, and calcium salts of carboxylic acids and calcium oxide are more preferred.

20 One type of the component (B) may be used alone, or two or more types may be used in combination.

[0032]

- Component (C): acid

The component (C) in the present invention is at least one acid selected from the group consisting of sulfuric acid, hydrochloric acid and phosphoric acid.

25

Among the component (C), from the viewpoint of stably expressing the catalytic activity, sulfuric acid is preferred. For the sulfuric acid, concentrated sulfuric acid may be used, or dilute sulfuric acid may be used.

[0033]

- 5 For the catalyst (α), for example, it is possible to use a fatty acid alkyl ester represented by the general formula (2) as the component (A), a calcium salt of carboxylic acid or calcium oxide as the component (B), and sulfuric acid as the component (C).

[0034]

[Production method of catalyst (α)]

- 10 Examples of the method for producing the catalyst (α) include a method having a dispersion step of obtaining a dispersion by dispersing the component (B) in the component (A), and a mixing step of mixing the component (B) and the component (C) in the component (A) by adding the component (C) to the aforementioned dispersion.

[0035]

- 15 - Dispersion step

In the dispersion step, for example, a reactor equipped with a mixing tank having a jacket and a stirring tank provided with a paddle stirring blade is used. In the dispersion step, the component (A) and the component (B) are charged into the stirring tank, and they are stirred therein.

- 20 The temperature condition in this step is not particularly limited, but may be set to normal temperature (5 to 35°C), for example. The temperature adjustment inside the stirring tank is carried out, for example, by allowing a heating medium (such as water) at an arbitrary temperature to flow through inside the jacket.

- The stirring time in this step is not particularly limited, and is defined as the
25 time during which the component (B) is dispersed substantially uniformly in the

component (A). The stirring time in this step is, for example, from 10 to 60 minutes. The expression “substantially uniform” refers to a state in which there are no lumps of the component (B) or the like and it can be determined that the component (B) is uniformly dispersed by visual observation.

5 [0036]

- Mixing step

In the mixing step, the component (C) is added to and mixed with the dispersion obtained in the dispersion step to form a reaction product of the component (B) and the component (C), that is, an alkaline earth metal salt which is the main catalytically active
10 component, thereby obtaining an alkoxylation catalyst in which the catalytically active component is dispersed in the component (A).

The mixing method in this step is not particularly limited, although, for example, a method of dropwise adding the component (C) into the dispersion while stirring the dispersion inside the stirring tank is preferred.

15 The temperature condition in this step, that is, the reaction temperature is preferably from 10 to 60°C, and more preferably from 20 to 50°C. The lower limit of the reaction temperature is preferably 10°C and more preferably 20°C, and the upper limit thereof is preferably 60°C and more preferably 50°C. If the reaction temperature is less than the preferred lower limit described above, there is a possibility that the
20 reaction of the component (B) and the component (C) becomes too slow, thereby lowering the production efficiency of the catalyst (α). If the reaction temperature is greater than the preferred upper limit described above, there is a possibility that the catalytic activity of the resulting catalyst (α) becomes lower.

Adjustment of the reaction temperature is carried out, for example, by allowing
25 a heating medium (such as water) at an arbitrary temperature to flow through inside the

jacket.

The stirring time in this step (that is, reaction time) is a time in which the component (B) and the component (C) can be reacted sufficiently, and is a time in which the heat generation due to the addition of the component (C) can be controlled. For example, it is 1 to 2 hours. The stirring time in this step refers to a time after the addition of the component (C).

[0037]

The molar ratio expressed by the formula: component (C)/component (B) (hereinafter, also referred to as a "C/B ratio") in the mixing step is preferably at least 0.8 and less than 1, and more preferably from 0.9 to 0.98. The lower limit of the C/B ratio is preferably 0.8 and more preferably 0.9, and the upper limit thereof is preferably less than 1, and more preferably 0.98.

If the C/B ratio is equal to or greater than the preferred lower limit described above, the resulting catalyst (α) can satisfactorily reduce the amount of generated by-products in the production step of the fatty acid alkyl ester alkoxylate.

If the C/B ratio is equal to or greater than 0.9, the distribution of the number of moles of alkylene oxide added in the fatty acid alkyl ester alkoxylate obtained in the production method of the fatty acid alkyl ester alkoxylate is easily widened.

[0038]

The distribution of the number of moles of alkylene oxide added in a fatty acid alkyl ester alkoxylate can be determined by a gas chromatography method (also referred to as a GC method). The distribution of the number of moles of alkylene oxide added in a fatty acid alkyl ester alkoxylate is a value obtained by, for example, measuring the fatty acid alkyl ester alkoxylate by the gas chromatography method (also referred to as the GC method), summing areas of the maximum peak and the two peaks before and after the

maximum peak, among the resulting peaks derived from the fatty acid alkyl ester alkoxyate, and dividing the summed value by the total peak area. In those cases where a plurality of types of fatty acid alkyl ester alkoxyates are included, the distribution is defined as a value obtained by, for example, dividing the sum of areas of the maximum
 5 peak and the two peaks before and after the maximum peak, among the resulting peaks derived from the fatty acid alkyl ester alkoxyates, by the total peak area.

In order to widen the distribution of the number of moles of alkylene oxide added, the C/B ratio is more preferably equal to or greater than 0.93.

If the C/B ratio is equal to or less than the preferred upper limit described above,
 10 the catalytic activity of the resulting catalyst (α) is enhanced, and fatty acid alkyl ester alkoxyates can be produced efficiently. If the C/B ratio is less than 1, the catalytic activity of the resulting catalyst (α) can be significantly enhanced.

[0039]

Further, the mass ratio represented by the formula: [component (B) + component
 15 (C)]/component (A) (hereinafter, also referred to as a “(B + C)/A ratio”) in this step is preferably from 1/3 to 1, and more preferably from 1/2.5 to 1 or less. The lower limit of the (B + C)/A ratio is preferably 1/3 and more preferably 1/2.5, and the upper limit thereof is preferably 1.

If the (B + C)/A ratio is equal to or less than the preferred upper limit described
 20 above, stirring can be easily performed, and the component (B) and the component (C) can be mixed efficiently. If the (B + C)/A ratio is less than the preferred lower limit described above, the content of the catalytically active component in the component (A) is reduced, and the amount of the catalyst (α) added is increased excessively when producing the fatty acid alkyl ester alkoxyate, which is inefficient.

25 [0040]

- Other steps

After the mixing step, a catalyst aging step of stirring the catalyst (α) at an arbitrary temperature may be provided. The temperature condition in the catalyst aging step is, for example, preferably from 10 to 60°C, and more preferably from 20 to 50°C.

- 5 The lower limit of the above temperature condition is preferably 10°C and more preferably 20°C, and the upper limit thereof is preferably 60°C and more preferably 50°C. By providing the present step, the amount of unreacted component (B) can be reduced.

The stirring time in this step is, for example, from 0.5 to 3 hours.

[0041]

- 10 Furthermore, the catalyst (α) may be filtered, allowed to stand for separation, or the like to enhance the concentration of the catalytically active component in the catalyst (α).

[0042]

<Method for producing fatty acid alkyl ester alkoxylate>

- 15 An embodiment of a method for producing a fatty acid alkyl ester alkoxylate according to the present invention will be described below.

- The method for producing a fatty acid alkyl ester alkoxylate according to the present embodiment is a method of adding 5 to 25 moles of an alkylene oxide relative to 1 mole of a fatty acid alkyl ester represented by the general formula (I) in the presence of
- 20 a specific alkoxylation catalyst (catalyst (α)) and a certain amount of monohydric/dihydric alcohol, and examples thereof include a production method having a catalyst dispersion step, an addition reaction step and an aging step.

[0043]

<<Catalyst dispersion step>>

- 25 The catalyst dispersion step is a step of dispersing the catalyst (α) in a mixture

of a fatty acid alkyl ester represented by the general formula (I) serving as the starting material, and a certain amount of monohydric/dihydric alcohol. In this step, the fatty acid alkyl ester, the catalyst (α), and a certain amount of the monohydric/dihydric alcohol are mixed.

5 In this step, for example, a stirring tank reactor is used.

[0044]

The mixing ratio of the fatty acid alkyl ester and the monohydric/dihydric alcohol in the catalyst dispersion step is such that the amount of the monohydric/dihydric alcohol is from 0.05 to 0.20 moles, and preferably at least 0.06 moles and not more than
10 0.10 moles, relative to 1 kg of the fatty acid alkyl ester. The lower limit of the amount of the monohydric/dihydric alcohol, relative to 1 kg of the fatty acid alkyl ester, is 0.05 moles and preferably 0.06 moles, and the upper limit thereof is 0.20 moles and preferably 0.10 moles.

If the amount (mole) of the monohydric/dihydric alcohol relative to 1 kg of the
15 fatty acid alkyl ester is equal to or greater than the lower limit described above, a fatty acid alkyl ester alkoxylate useful as a cleaning component of a liquid detergent that exhibits favorable fluidity in low temperature conditions can be produced. This effect reaches a plateau when the amount exceeds the above upper limit. If the amount is equal to or less than the upper limit described above, an increase in cost can be
20 suppressed. In addition, if the amount exceeds the above upper limit, the distribution of the number of moles of alkylene oxide added becomes too narrow in some cases.

[0045]

It should be noted that when using the catalyst (α), the component (A) is also introduced together with the catalytically active component.

25 In those cases where the component (A) contains the fatty acid alkyl ester

represented by the formula (I), the fatty acid alkyl ester serving as the starting material in this step includes the fatty acid alkyl ester corresponding to the above formula (I) which originates from the component (A). In other words, the amount of the fatty acid alkyl ester serving as the starting material is equal to the amount of fatty acid alkyl ester

5 obtained by summing the amount of the fatty acid alkyl ester corresponding to the above formula (I) which originates from the component (A) and the amount of the fatty acid alkyl ester corresponding to the above formula (I) which is newly added in the catalyst dispersion step.

If the component (A) contains the monohydric/dihydric alcohol, the
 10 monohydric/dihydric alcohol used in a certain amount in this step includes the monohydric/dihydric alcohol originated from the component (A). In other words, the combined amount of the monohydric/dihydric alcohol originated from the component (A) and the monohydric/dihydric alcohol newly added in the catalyst dispersion step is from 0.05 to 0.20 moles, relative to 1 kg of the fatty acid alkyl ester.

15 [0046]

The amount of the catalyst added to the raw material can be determined from the amount of metal in the catalyst (α), and the metal content is preferably from 0.01 to 0.25 moles and more preferably from 0.02 moles to 0.10 moles, relative to 1 kg of the fatty acid alkyl ester serving as the raw material.

20 [0047]

<<Addition reaction step>>

The addition reaction step is a step of adding 5 to 25 moles of an alkylene oxide relative to 1 mole of the fatty acid alkyl ester represented by the general formula (I) in the presence of a specific alkoxylation catalyst (catalyst (α)) and a certain amount of
 25 monohydric/dihydric alcohol to obtain a fatty acid alkyl ester alkoxylate. This step

includes a step of performing an operation of setting to arbitrary temperature and pressure conditions (condition setting operation) for the addition reaction, followed by a step of performing an operation of bringing an alkylene oxide (hereinafter, may be referred to as AO) into contact with a mixture of the fatty acid alkyl ester, the catalyst (α) and a certain amount of monohydric/dihydric alcohol (AO contact operation).

[0048]

Step of performing condition setting operation:

In this step, the temperature and pressure conditions are set to those appropriate for the addition reaction. The temperature condition for the addition reaction (addition reaction temperature) is, for example, preferably from 150 to 180°C, and more preferably from 160 to 180°C.

The pressure condition for the addition reaction is suitably determined in consideration of the addition reaction temperature, and is, for example, preferably from 0.1 to 1 MPa, and more preferably from 0.1 MPa to 0.6 MPa. The lower limit of the above pressure condition is preferably 0.1, and the upper limit thereof is preferably 1 MPa and more preferably 0.6 MPa.

[0049]

Step of performing AO contact operation:

In this step, an alkylene oxide is brought into contact with a mixture of the fatty acid alkyl ester, the catalyst (α) and a certain amount of monohydric/dihydric alcohol which is obtained in the catalyst dispersion step described above. The amount of AO introduced with respect to 1 mole of the fatty acid alkyl ester represented by the formula (I) in the AO contact operation is from 5 to 25 moles, and preferably from 10 to 20 moles. The lower limit of the aforementioned amount of introduced AO is 5 moles and preferably 10 moles, and the upper limit thereof is 25 moles and preferably 20 moles.

As the number of moles of AO added increases, that is, as the amount of introduced AO increases, the amount of the generated high molecular weight polyethylene glycol increases.

[0050]

5 <<Aging step>>

The aging step is a step of stirring in the stirring tank, that is, the reaction product at an arbitrary temperature after the addition reaction step. By providing the present step, it is possible to reduce the amount of unreacted fatty acid alkyl esters and the amount of unreacted AO. The temperature condition of the present step is, for
10 example, preferably from 150 to 180°C, more preferably from 160 to 180°C, and still more preferably the same as the addition reaction temperature. The stirring time in the aging step is preferably from 10 to 20 minutes, and more preferably from 30 to 60 minutes.

[0051]

15 The production method according to the present embodiment may have, if necessary, a purification step for removing the catalytically active components and the like remaining in the fatty acid alkyl ester alkoxylate, in addition to the catalyst dispersion step, the addition reaction step and the aging step. Examples of the method for removing the catalytically active components and the like include methods by
20 washing with water, centrifugation, filtration, or the like.

Among them, it is preferable to perform washing with water and centrifugation.

In the purification step, for example, the reaction product obtained in the aging step is dissolved by heating to 70 to 120°C, 5 to 30 parts by mass of purified water is added relative to 100 parts by mass of the reaction product, and the resulting mixture is
25 stirred for 30 to 120 minutes. Then, the resultant was cooled to 50 to 70°C, and further

stirred for 30 to 120 minutes. Thereafter, the catalytically active components and the like are removed by centrifugation.

[0052]

In the production method according to the present embodiment described above,
5 the total amount of the monohydric/dihydric alcohol is mixed in the catalyst dispersion step. However, the configuration is not limited thereto, and the total amount of the monohydric/dihydric alcohol may be mixed during the condition setting operation in the addition reaction step; or a portion of the monohydric/dihydric alcohol may be mixed in the catalyst dispersion step, while the remainder of the monohydric/dihydric alcohol may
10 be mixed during the condition setting operation in the addition reaction step.

In any case, before the AO contact operation, that is, at the time of adding an alkylene oxide to the fatty acid alkyl ester, the mixing ratio of the fatty acid alkyl ester and the monohydric/dihydric alcohol is such that the amount of the monohydric/dihydric alcohol is from 0.05 to 0.20 moles, relative to 1 kg of the fatty acid alkyl ester.

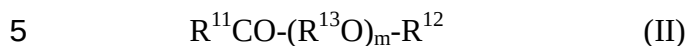
15 [0053]

In the method for producing a fatty acid alkyl ester alkoxylate according to the present invention, 5 to 25 moles of an alkylene oxide is added relative to 1 mole of the fatty acid alkyl ester represented by the general formula (I) in the presence of a specific alkoxylation catalyst and 0.05 to 0.20 moles of the monohydric/dihydric alcohol relative
20 to 1 kg of the fatty acid alkyl ester represented by the general formula (I). As described above, according to such a production method, since the addition reaction step is carried out in the presence of a certain amount of monohydric/dihydric alcohol, a fatty acid alkyl ester alkoxylate useful as a cleaning component of a liquid detergent that exhibits favorable fluidity in low temperature conditions can be produced.

25 [0054]

(Fatty acid alkyl ester alkoxylate)

According to the production method of the present invention, a fatty acid alkyl ester alkoxylate represented by the following general formula (II) is produced in a favorable manner.



[In the formula (II), R^{11} is a hydrocarbon group of 7 to 17 carbon atoms, R^{12} is a linear alkyl group of 1 to 3 carbon atoms, $R^{13}O$ is an oxyalkylene group of 2 to 4 carbon atoms, and m represents the average number of repetitions of $R^{13}O$, and is a number from 5 to 25.

10 [0055]

In the aforementioned formula (II), R^{11} and R^{12} are the same as R^{11} and R^{12} , respectively, in the above formula (I).

$R^{13}O$ is an oxyethylene group, an oxypropylene group or an oxybutylene group. $(R^{13}O)_m$ may be a mixture of two or more types of oxyalkylene groups composed of an oxyethylene group, an oxypropylene group and an oxybutylene group. When two or more types of oxyalkylene groups are mixed, the oxyalkylene groups may be mixed in a block form, or may be mixed in a random form. Among them, as the oxyalkylene group, an oxyethylene group is preferred.

m is a number from 5 to 25, and is preferably a number from 9 to 20. It should be noted that m represents the “average” number of repetitions of the oxyalkylene group. In other words, the compound represented by the general formula (II) is an assembly of molecules with different numbers of repetition of oxyalkylene groups. Further, the fatty acid alkyl ester alkoxylate produced by the method of the present invention may be an assembly of molecules with different types of R^{11} . R^{11} or R^{12} in each of the molecules constituting the above assembly of molecules may be the same or different from each

other.

[0056]

The fatty acid alkyl ester alkoxylate produced by the above production method is useful as a cleaning component of a liquid detergent, and the liquid detergent

5 containing this as a cleaning component exhibits favorable fluidity in low temperature conditions.

[0057]

(Liquid detergent)

The fatty acid alkyl ester alkoxylate produced by the production method of the
10 present invention is suitably used for a liquid detergent. The liquid detergent containing the fatty acid alkyl ester alkoxylate produced by the production method of the present invention can be applied for home use or industrial use, is suitable as a liquid detergent for clothing, and is particularly suitable as a concentrated type of liquid detergent for clothing with a high surfactant concentration.

15 [0058]

The content of the fatty acid alkyl ester alkoxylate in a liquid detergent is preferably from 10 to 50% by mass, and more preferably from 30 to 50% by mass, based on the total mass of the liquid detergent. The lower limit is preferably 10% by mass and more preferably 30% by mass, and the upper limit is preferably 50% by mass.

20 If the content of the fatty acid alkyl ester alkoxylate is equal to or more than the preferred lower limit described above, the fluidity under low temperature conditions increases. In addition, the detergency against dirt is enhanced. On the other hand, if the content of the fatty acid alkyl ester alkoxylate is equal to or less than the preferred upper limit described above, an increase in the viscosity of the liquid detergent under low
25 temperature conditions can be suppressed even further.

[0059]

As the other components included in the liquid detergent, for example, surfactants, chelating agents, alkali agents, antioxidants, enzymes, enzyme stabilizers, viscosity reducing agents or solubilizing agents, preservatives, metal oxides or metal salts, texture improvers, fluorescent whitening agents, anti-redeposition agents, soil releasing agents, pearling agents, bleaching agents, flavoring agents, coloring agents, emulsifying agents, extracts of natural products or the like, pH adjusting agents, and the like can be used.

[0060]

The liquid detergent containing the fatty acid alkyl ester alkoxylate produced by the production method of the present invention is unlikely to solidify in low temperature conditions and exhibits favorable fluidity. For this reason, it is possible to sell and use such a liquid detergent in a wide area as a product to be launched in the market.

[Examples]

[0061]

The present invention will be described below in more detail based on a series of examples and comparative examples. However, the present invention is in no way limited by the following examples. It should be noted that in the present example, unless stated otherwise, “%” refers to “% by mass.”

The following raw materials were used in the present example.

[0062]

- Fatty acid alkyl ester

Methyl laurate: “PASTELL M-12” (trade name), manufactured by Lion

Chemical Co., Ltd.

Methyl myristate: "PASTELL M-14" (trade name), manufactured by Lion Chemical Co., Ltd.

[0063]

- Alkylene oxide

5 Ethylene oxide: manufactured by Air Water Inc.

[0064]

- Alkoxylation catalyst

Catalysts (α -1), (α -2), (α -3), (α -4) and (β) synthesized by the production method described later.

10 [0065]

- Monohydric/dihydric alcohol

2-EH: 2-ethylhexanol, a reagent manufactured by Junsei Chemical Co., Ltd.

2-PrOH: 2-propanol, an extra pure reagent manufactured by Kanto Chemical Co., Inc.

15 [0066]

- Components incorporated in liquid detergent

a-1-1 to a-1-12: Fatty acid alkyl ester alkoxyates produced by the production methods of Examples 1 to 7 and Comparative Examples 1 to 5 (fatty acid methyl ester ethoxyates (MEE), average number of moles of EO added: 15). A mixture of those in
20 which R¹¹ in the above general formula (II) is an alkyl group of 11 carbon atoms and those in which R¹¹ in the above general formula (II) is an alkyl group of 13 carbon atoms. A compound represented by the formula (II) in which R¹² is a methyl group, R¹³O is an oxyethylene group, and m is 15.

[0067]

25 a-2: A product obtained by adding an average of 15 molar equivalents of

ethylene oxide to the natural alcohol CO-1217 (trade name) manufactured by the Protector & Gamble Company.

[Synthesis of a-2]

224.4 g of the natural alcohol CO-1270 manufactured by the Protector &
5 Gamble Company and 2.0 g of a 30% by mass NaOH aqueous solution were collected in a pressure resistant reaction vessel, and the atmosphere inside the reaction vessel was replaced with nitrogen. Next, dehydration was carried out for 30 minutes at a temperature of 100°C and a pressure of 2.0 kPa or below, and the temperature was then raised to 160°C. Then, while stirring, 760.4 g of (gaseous) ethylene oxide was
10 gradually added into the alcohol solution using a blowing tube, while adjusting the addition rate so that the reaction temperature did not exceed 180°C. After completion of the addition of ethylene oxide, the resulting mixture was aged for 30 minutes at a temperature of 180°C and a pressure of 0.3 MPa or below. Then, unreacted ethylene oxide was evaporated for 10 minutes at a temperature of 180°C and a pressure of 6.0 kPa
15 or below. Next, after the temperature was cooled to 100°C or below, 70% by mass of p-toluene sulfonic acid was added for neutralization so that an aqueous solution containing 1% by mass of the resulting reaction product had a pH value of approximately 7, thereby obtaining the product a-2.

[0068]

20 b-1: coconut fatty acid, manufactured by NOF Corporation.

e-1: methylglycinediacetic acid trisodium salt (MGDA), "Trilon M" (trade name), manufactured by BASF Corporation.

Protease: "Coronase 48L" (trade name), manufactured by Novozymes A/S.

SR agent: soil releasing agent, "TexCare SRN-170C" (trade name),
25 manufactured by Clariant Japan K.K.

LAS-H: a linear alkylbenzene sulfonic acid, “Lipon LH-200” (trade name),
manufactured by Lion Corporation.

MEA: monoethanolamine, manufactured by Nippon Shokubai Co., Ltd.

BHT: dibutylhydroxytoluene, “SUMILZER BHT-R” (trade name),
5 manufactured by Sumitomo Chemical Co., Ltd.

Citric acid: “citric acid” (trade name), manufactured by Kanto Chemical Co.,
Inc.

Ethanol: “Specific Alcohol 95% Synthesized” (trade name), manufactured by Japan
Alcohol Trading Co., Ltd.

10 Sodium lactate: “sodium lactate” (trade name), manufactured by Kanto
Chemical Co., Inc.

Fragrance: A fragrance composition A disclosed in Tables 11 to 18 of Japanese
Unexamined Patent Application, First Publication No. 2002-146399

Dye: Green No. 3, “Green No. 3” (trade name), manufactured by Kishi Kasei
15 Co., Ltd.

pH adjusting agents: sulfuric acid, sodium hydroxide, potassium hydroxide,
monoethanolamine.

[0069]

<Production of alkoxylation catalyst>

20 Raw materials shown below (a liquid dispersion medium, an alkaline earth
metal compound and sulfuric acid) were used.

Liquid dispersion medium: a fatty acid methyl ester mixture solution of a lauric
acid methyl ester and a myristic acid methyl ester, Pastell M 124 (trade name),
manufactured by Lion Chemicals Co., Ltd.

25 Alkaline earth metal compound: calcium acetate monohydrate, guaranteed

reagent, manufactured by Kanto Chemical Co., Inc.

Calcium oxide, guaranteed reagent, manufactured by Wako Pure Chemical Industries, Ltd.

Barium oxide, guaranteed reagent, manufactured by Wako Pure Chemical Industries, Ltd.

Sulfuric acid: guaranteed reagent, concentration of 96% by mass, manufactured by Kanto Chemical Co., Inc.

[0070]

By mixing the above alkaline earth metal compound and sulfuric acid in the liquid dispersion medium, a catalyst (α -1), a catalyst (α -2), a catalyst (α -3), a catalyst (α -4) and a catalyst (β) that were alkoxylation catalysts were prepared. C/B ratios of the catalysts (α -1), (α -2), (α -3), (α -4) and (β) were 0.90, 0.96, 0.90, 0.90 and 0.67, respectively, and (B + C)/A ratios thereof were 0.46, 0.47, 0.41, 0.40 and 0.42, respectively. It should be noted that the incorporated amounts of the components listed below are the converted amounts as pure components.

Production methods of catalysts (α -1), (α -2) and (β)

More specifically, the fatty acid methyl ester mixture solution and calcium acetate monohydrate were placed in a 500 mL beaker and mixed at room temperature (25°C) using a paddle stirring blade to obtain a dispersion (dispersion step).

While stirring the dispersion, 96% by mass of sulfuric acid was added and mixed over 10 minutes using a dropping funnel (mixing step). In the mixing step, since heat is generated by the addition of sulfuric acid, the beaker was cooled in a water bath, and the resulting mixture was stirred for 1 hour while controlling the reaction temperature at 20 to 50°C.

After the addition of sulfuric acid, the resulting mixture was further stirred for 2

hours while maintaining the temperature at 20 to 50°C, thereby obtaining alkoxylation catalysts (catalyst (α -1), catalyst (α -2), and catalyst (β)) (catalyst aging step).

Production method of catalyst (α -3)

More specifically, the fatty acid methyl ester mixture solution and calcium oxide
 5 were placed in a 500 mL beaker and mixed at room temperature (25°C) using a paddle stirring blade to obtain a dispersion (dispersion step).

While stirring the dispersion, sulfuric acid diluted to 76% was added and mixed over 10 minutes using a dropping funnel (mixing step). In the mixing step, since heat is generated by the addition of sulfuric acid, the beaker was cooled in a water bath, and the
 10 resulting mixture was stirred for 1 hour while controlling the reaction temperature at 20 to 50°C.

After the addition of sulfuric acid, the resulting mixture was further stirred for 2 hours while maintaining the temperature at 20 to 50°C, thereby obtaining an alkoxylation catalyst (catalyst (α -3) (catalyst aging step).

15 Production method of catalyst (α -4)

A catalyst (α -4) was obtained using the same production method as that described above for the catalyst (α -3), with the exception of using barium oxide instead of calcium oxide.

It should be noted that the amount of the compound used is as described in Table
 20 1.

[0071]

<Production of fatty acid alkyl ester alkoxylate>

(Examples 1 to 7, Comparative Examples 3 to 5)

After placing 12.5 g of the alkoxylation catalyst (the catalyst (α -1), the catalyst
 25 (α -2), the catalyst (α -3), the catalyst (α -4), or the catalyst (β)) obtained above, 462 g of

the above methyl laurate and 166 g of the above methyl myristate in an autoclave, a predetermined amount of monohydric/dihydric alcohol shown in Table 1 was added thereto, and the resulting mixture was stirred at room temperature (20°C) (catalyst dispersion step).

5 While stirring the mixture, the atmosphere inside the autoclave was replaced with nitrogen. Then, the temperature was raised to the ethylene oxide (EO) addition reaction temperature (160°C), and the pressure was adjusted to 0.1 to 0.5 MPa (condition setting operation). Subsequently, under such temperature and pressure conditions, 1,876 g of ethylene oxide (EO) (15 times the number of moles, based on the combined
10 total of methyl laurate and methyl myristate) was introduced thereto, and the reaction was allowed to proceed with stirring (EO contact operation) (the process described up to this point constitutes the addition reaction step).

Then, the resultant was stirred for 0.5 hours at the aforementioned EO addition reaction temperature (aging step). Thereafter, the resultant was cooled to 80°C to obtain
15 2,516 g of a crude reaction product.

Subsequently, 29.3 g of purified water was added to 250 g of the crude reaction product which was dissolved by heating to 80°C, and the resulting mixture was stirred 30 minutes while maintaining the temperature at 80°C. Then, the resultant was cooled to 50°C, and the stirring was continued for an additional 30 minutes. Then, the catalyst
20 and aggregates were removed by centrifugation, and the resultant was subjected to purification (purification step).

By the production methods described above, targeted fatty acid methyl ester ethoxylates (MEE) a-1-1 to a-1-7 and a-1-10 to a-1-12 were obtained, respectively.

[0072]

25 (Comparative Example 1)

A targeted fatty acid alkyl ester alkoxyate a-1-8 was obtained in the same manner as in Example 1 with the exception that no monohydric/dihydric alcohol was added.

[0073]

5 (Comparative Example 2)

A product obtained by adding an average of 15 molar equivalents of ethylene oxide to 2-ethylhexanol (15-EO adduct of 2-EH) was synthesized.

The alkoxylation catalyst (α -1) obtained above was filtered and thoroughly washed with acetone, and then the resulting solid was dried at 50°C. 2.0 g of the solid
10 of the alkoxylation catalyst obtained above and 285 g of 2-ethylhexanol were placed in an autoclave and then stirred at room temperature (20°C).

While stirring the mixture, the atmosphere inside the autoclave was replaced with nitrogen. Then, the temperature was raised to the ethylene oxide (EO) addition reaction temperature (160°C), and the pressure was adjusted to 0.1 to 0.5 MPa (condition
15 setting operation). Subsequently, under such temperature and pressure conditions, 1,447 g of ethylene oxide (EO) (15 times the number of moles of 2-ethylhexanol) was introduced thereto, and the reaction was allowed to proceed with stirring.

Then, the resultant was stirred for 0.5 hours at the aforementioned EO addition reaction temperature. Thereafter, the resultant was cooled to 80°C to obtain 1,734 g of a
20 crude reaction product.

Subsequently, 250 g of the crude reaction product which was dissolved by heating to 50°C was filtered to remove the catalyst, and the resultant was subjected to purification to obtain a 15-EO adduct of 2-EH.

Then, the fatty acid alkyl ester alkoxyate produced by the method of
25 Comparative Example 1, and 0.06 moles of the 15-EO adduct of 2-EH relative to 1 kg of

this fatty acid alkyl ester alkoxylate were mixed (15-EO adduct of 2-EH was added later)
to obtain a product a-1-9.

[0074]

[Table 1]

5

10

15

20

25

[0075]

<Production of liquid detergent>

(Test Example 1)

According to the blending composition shown in Table 2, 1,000 g of a liquid
5 detergent was prepared by a conventional method (if there was a component which was
not yet added, the component was not added).

[0076]

(Test Examples 2 to 12)

1,000 g of liquid detergents were produced in the same manner as in Test
10 Example 1 with the exception of changing the fatty acid methyl ester ethoxylate (MEE)
from a-1-1 to a-1-2 to a-1-12, respectively.

[0077]

Units of the incorporated amounts in Table 2 are percent by mass, and indicate,
for all the components, the converted amounts as pure components. It should be noted
15 that the liquid detergent in each example was prepared by adding water as a balance so
that the sum of the components described in the table will be 100% by mass.

In the liquid detergent in each example, by respectively adding an appropriate
amount of pH adjusting agent, the pH at 25°C was adjusted to 7.0. For the pH of the
liquid detergent, the temperature of the liquid detergent was adjusted to 25°C, and by
20 using a glass electrode type pH meter (product name: HM-30G, manufactured by DKK-
TOA Corporation), the glass electrode was directly immersed in the above liquid
detergent, and the value shown after one minute was measured.

[0078]

<Evaluation>

25 For the liquid detergent in each example, the fluidity of the liquid detergent was

evaluated by the evaluation method described below. The results are shown in Table 2.

[0079]

[Evaluation of fluidity of liquid detergent]

100 mL of the liquid detergent in each example was respectively collected in a
5 transparent glass bottle (standard wide mouth bottle PS-NO. 11), and was sealed by
closing the lid. In this state, the sealed glass bottle was allowed to stand in a constant
temperature bath at -5°C and stored for 1 month.

After such storage, the aforementioned glass bottle was taken out from the
constant temperature bath at -5°C, changes in the liquid surface were visually observed
10 by horizontally bringing down the aforementioned glass bottle that had been stored at -
5°C, and the fluidity of the liquid detergent was evaluated based on the following
evaluation criteria.

Evaluation criteria

A: The liquid surface became horizontal within 10 seconds after horizontally
15 bringing down the aforementioned glass bottle.

B: It took more than 10 seconds for the liquid surface to become horizontal after
horizontally bringing down the aforementioned glass bottle.

C: The fluidity was not observed at all because of solidification.

[0080]

20 [Table 2]

Liquid detergent	Test Examples											
	1	2	3	4	5	6	7	8	9	10	11	12
a-1-1	38											
a-1-2		38										
a-1-3			38									
a-1-4				38								
a-1-5					38							
a-1-6						38						
a-1-7							38					
a-1-8								38				
a-1-9									38			
a-1-10										38		
a-1-11											38	
a-1-12												38
a-2	5	5	5	5	5	5	5	5	5	5	5	5
b-1	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
e-1	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Protease	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
SR agent	1	1	1	1	1	1	1	1	1	1	1	1
LAS-H	8	8	8	8	8	8	8	8	8	8	8	8
MEA	1	1	1	1	1	1	1	1	1	1	1	1
BHT	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Citric acid	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Ethanol	8	8	8	8	8	8	8	8	8	8	8	8
Sodium lactate	1	1	1	1	1	1	1	1	1	1	1	1
Fragrance	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Dye	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005
pH adjusting agent	Appropriate amount	Appropriate amount	Appropriate amount	Appropriate amount	Appropriate amount	Appropriate amount	Appropriate amount	Appropriate amount	Appropriate amount	Appropriate amount	Appropriate amount	Appropriate amount
Water	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance
Total (% by mass)	100	100	100	100	100	100	100	100	100	100	100	100
Fluidity of liquid detergent	A	A	A	A	A	A	A	C	C	B	B	B
Time taken until liquid surface became horizontal (seconds)	10	5	5	3	1	2	5	-	-	14	13	20

[0081]

From the results shown in Table 2, it was confirmed that the liquid detergents of Test Examples 1 to 7 containing the fatty acid alkyl ester alkoxylates produced by the production methods of Examples 1 to 7 according to the present invention exhibited
5 favorable fluidity under low temperature conditions.

In addition, it was also confirmed that the fatty acid alkyl ester alkoxylates produced by the production methods of Examples 1 to 7 according to the present invention were useful as cleaning components of liquid detergents.

[0082]

10 Hereinafter, solidification characteristics at low temperatures of a liquid detergent using a fatty acid alkyl ester alkoxylate produced by a sulfuric acid/alkaline earth metal-based catalyst and a liquid detergent using a fatty acid alkyl ester alkoxylate produced by the aforementioned composite metal oxide catalyst will be described with reference to Examples and Comparative Examples.

15 [0083]

(Example 3, Test Example 3)

For comparison, Example 3 in which a fatty acid alkyl ester alkoxylate was produced by the sulfuric acid/alkaline earth metal-based catalyst and the liquid detergent of Test Example 3 which was produced using the fatty acid alkyl ester alkoxylate a-1-3
20 obtained in Example 3 are described in Table 3 and Table 4. The distribution of the number of moles of ethylene oxide added in the fatty acid alkyl ester alkoxylate a-1-3 which was measured by the following GC method was 54%.

[0084]

(Comparative Example 6, Test Example 13) Liquid detergent using fatty acid alkyl ester
25 alkoxylate prepared by composite metal oxide catalyst

(Comparative Example 6)

A fatty acid alkyl ester alkoxylate was produced by a composite metal oxide catalyst.

Aluminum magnesium hydroxide having a chemical composition of
 5 $2.5\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot \text{mH}_2\text{O}$ (KYOWAAD 300, manufactured by Kyowa Chemical Industry Co., Ltd.) was calcined for 3 hours at 900°C to obtain a magnesium/aluminum composite metal oxide catalyst powder (catalyst γ).

After charging 184.1 kg (859 mol) of methyl laurate (PASTELL M-12, manufactured by Lion Chemicals Co., Ltd.), 66.0 kg (272 mol) of methyl myristate
 10 (PASTELL M-14, manufactured by Lion Chemicals Co., Ltd.), 1.00 kg of the aforementioned composite metal catalyst and 1.25 kg of glycerin as a polyhydric alcohol into a 2,000 kL stirring reaction tank, 0.05 kg of potassium hydroxide was added thereto, and the resulting mixture was stirred for 10 minutes to carry out an alkaline denaturation treatment of the catalyst. Thereafter, while stirring and mixing, the atmosphere inside
 15 the reaction tank was replaced with nitrogen and heated up to 100°C, and dehydration was carried out for 30 minutes under a reduced pressure condition of not more than 1.3 kPa. Then, the temperature was raised to 180°C, and under a condition in which the pressure upper limit was 0.49 MPa, 747.6 kg (16,972 mol, 15 times the number of moles of the fatty acid methyl ester) of ethylene oxide was introduced thereto. After further
 20 conducting an aging reaction for 0.5 hours, the resultant was cooled to 80°C and taken out to obtain 999 kg of a crude reaction product containing an alkylene oxide adduct, that is, a fatty acid alkyl ester alkoxylate a-1-13. The average number of moles of ethylene oxide added in the fatty acid alkyl ester alkoxylate a-1-13 was 15, and the distribution of the number of moles of ethylene oxide added which was measured by the following GC
 25 method was 54%. Further, 0.9% by weight of polyethylene glycol as a by-product was

contained in the fatty acid alkyl ester alkoxylate a-1-13.

(Test Example 13)

1,000 g of a liquid detergent was produced in the same manner as in Example 1 with the exception of changing the fatty acid methyl ester ethoxylate (MEE) from a-1-1
5 to a-1-13.

[0085]

(Comparative Example 7, Test Example 14) Liquid detergent using a fatty acid alkyl ester alkoxylate produced by a sulfuric acid/alkaline earth metal-based catalyst without the addition of a certain amount of monohydric/dihydric alcohol.

10 (Comparative Example 7)

In the production of a fatty acid alkyl ester alkoxylate, a fatty acid alkyl ester alkoxylate a-1-14 was produced in the same manner as in Example 3 of the present invention that produced the fatty acid alkyl ester alkoxylate a-1-3, with the exceptions of not adding isopropanol used as the certain amount of monohydric/dihydric alcohol and
15 adding 0.06 moles of glycerol relative to 1 kg of the fatty acid alkyl ester. The average number of moles of ethylene oxide added in the fatty acid alkyl ester alkoxylate a-1-14 was 15, and the distribution of the number of moles of ethylene oxide added which was measured by the following GC method was 54%.

(Test Example 14)

20 1,000 g of a liquid detergent was produced in the same manner as in Example 1 with the exception of changing the fatty acid methyl ester ethoxylate (MEE) from a-1-1 to a-1-14.

[0086]

[Measurement and calculation of the distribution of the number of moles of alkylene
25 oxide added by the gas chromatography method]

The distribution of the number of moles of ethylene oxide added (also referred to as the molar distribution of the EO addition) in the crude reaction product was determined by the gas chromatography method (also referred to as the GC method).

The reaction samples were diluted with acetone so that the concentrations of the fatty acid alkyl ester alkoxylate solutions were 1% to prepare samples for analysis.

Conditions for the GC method are shown as the following measurement conditions, and the distribution of the number of moles of EO added (also referred to as GC area%) was calculated by the following calculation method. The smaller the value of the distribution of the number of moles of EO added, the wider the distribution of the number of moles of EO added.

(Measurement conditions for GC method)

- Gas chromatograph: GC-2025, manufactured by Shimadzu Corporation
- Column: DB-1 HT manufactured by Agilent Technologies, Inc., length: 30 m, inner diameter: 0.25 mm, film thickness: 0.1 μm
- Mobile phase: helium
- Detector: hydrogen flame ionization detector (FID), 380°C
- Inlet: split, 380°C
- Temperature: 100°C $\rightarrow$ 380°C

(Calculation method)

From the peak area of the peaks obtained by measuring the samples by the GC method, the molar distribution of the EO addition was calculated by the following equation.

$$\frac{\{(\text{Area of the maximum peak (P1) derived from methyl laurate ester alkoxylate}) + (\text{total area of the two peaks before and after the maximum peak P1}) + (\text{area of the maximum peak (P2) derived from methyl myristate ester alkoxylate}) + (\text{total area of the two peaks})\}}{\text{Total area of all peaks}} \times 100\%$$

before and after the maximum peak P2)) ÷ (total peak area)

[0087]

<Evaluation>

For the liquid detergent in each Reference Example, the fluidity of the liquid
5 detergent was evaluated by the same evaluation method as in Examples. The results are shown in Table 4.

[Table 3]

	Example	Comparative Example	
	3	6	7
Fatty acid alkyl ester	Methyl laurate		
	Methyl myristate		
Alkylene oxide	Ethylene oxide		
Catalyst	Catalyst (α -1)	Catalyst (γ)	Catalyst (α -1)
Alcohol	2-PrOH	-	-
Amount (mole) of monohydric/dihydric alcohol relative to 1 kg of fatty acid alkyl ester	0.06	-	-
(C)/(B) ratio	0.9	-	0.9
Distribution of number of moles of ethylene oxide added (%)	54	54	54
Fatty acid alkyl ester alkoxylate	a-1-3	a-1-13	a-1-14

10

15

[Table 4]

Liquid detergent		Test Examples		
		3	13	14
MEE	a-1-3	38		
	a-1-13		38	
	a-1-14			38
a-2		5	5	5
b-1		0.5	0.5	0.5
e-1		0.5	0.5	0.5
Protease		0.4	0.4	0.4
SR agent		1	1	1
LAS-H		8	8	8
MEA		1	1	1
BHT		0.1	0.1	0.1
Citric acid		0.01	0.01	0.01
Ethanol		8	8	8
Sodium lactate		1	1	1
Fragrance		0.5	0.5	0.5
Dye		0.0005	0.0005	0.0005
pH adjusting agent		Appropriate amount	Appropriate amount	Appropriate amount
Water		Balance	Balance	Balance
Total (% by mass)		100	100	100
Fluidity of liquid detergent		A	A	C
Time taken until liquid surface became horizontal (seconds)		5	1	-

[0088]

From the results shown in Tables 3 and 4, it became clear that a problem of easy
5 solidification of the liquid detergent under a low temperature condition of less than 0°C
is a specific problem occurring in the case of producing a liquid detergent using a sulfuric
acid/alkaline earth metal-based catalyst, and that this problem can be solved by the
present invention in which a certain amount of monohydric/dihydric alcohol was added.

Further, even when a certain amount of monohydric/dihydric alcohol was not
10 added, the distribution of the number of moles of alkylene oxide added did not change
significantly compared with the case where a certain amount of monohydric/dihydric
alcohol was added. Therefore, it became clear that the reason why the liquid detergent

using a fatty acid alkyl ester alkoxylate produced by adding a certain amount of monohydric/dihydric alcohol became difficult to solidify was not due to changes in the distribution of the number of moles of alkylene oxide added.

5 [Industrial Applicability]

[0089]

According to the present invention, by producing a fatty acid alkyl ester alkoxylate in a reaction system using an acid/alkaline earth metal compound catalyst and containing a certain amount of monohydric/dihydric alcohol, it is possible to produce a
10 fatty acid alkyl ester alkoxylate useful as a cleaning component of the liquid detergent which is difficult to solidify under low temperature conditions.

[CLAIMS]

[Claim 1]

A method for producing a fatty acid alkyl ester alkoxylate by adding an alkylene
 5 oxide to a fatty acid alkyl ester represented by the following general formula (I), the
 method comprising:

a step of adding 5 to 25 moles of said alkylene oxide relative to 1 mole of said
 fatty acid alkyl ester in the presence of an alkoxylation catalyst obtained by reacting an
 alkaline earth metal compound (B) and at least one acid (C) selected from the group
 10 consisting of sulfuric acid, hydrochloric acid and phosphoric acid in a liquid dispersion
 medium (A), and 0.05 to 0.20 moles of at least one alcohol selected from a group
 consisting of a monohydric alcohol and a dihydric alcohol with respect to 1 kg of said
 fatty acid alkyl ester,

wherein a molar ratio of said acid (C) to said alkaline earth metal compound (B)
 15 (C/B ratio) is equal to or more than 0.8 but less than 1.



wherein R^{11} is a hydrocarbon group of 7 to 17 carbon atoms, and R^{12} is a linear
 alkyl group of 1 to 3 carbon atoms.

20 [Claim 2]

The method for producing a fatty acid alkyl ester alkoxylate according to Claim
 1, wherein the molar ratio of said acid (C) to said alkaline earth metal compound (B)
 (C/B ratio) is from 0.9 to 0.98.

[Claim 3]

The method for producing a fatty acid alkyl ester alkoxylate according to Claim 1, wherein said alcohol is a linear or branched monohydric alcohol of 1 to 18 carbon atoms.