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(54) Title: CONTROLLED POLYALKOXYLATION METHOD OF FATTY AMINES

(57) Abstract: The present invention provides methods of preparing quaternary fatty ammonium polyalkoxylates having 2 (nearly) symmetrical alkoxylate chains in a one-pot reaction under anhydrous conditions comprising the steps of (i) alkoxylating a primary fatty amine under anhydrous conditions in the absence of a catalyst using a suitable alkoxylation agent to obtain a (nearly) symmetrical tertiary fatty amine N,N-alkoxylate, (ii) extending the N,N-alkoxylate groups by reacting the (nearly) symmetrical tertiary fatty amine N,N-alkoxylate with a suitable alkoxylation agent in the presence of a basic catalyst (under controlled temperature and pressure conditions) to obtain a (nearly) symmetrical tertiary fatty amine N,N- polyalkoxylate, and (iii) reacting the (nearly) symmetrical tertiary fatty amine N,N- polyalkoxylate with a suitable alkoxylation agent under neutral to acidic conditions to obtain the desired quaternary fatty ammonium polyalkoxylate.

Controlled Polyalkoxylation Method of Fatty Amines

Field of the Invention

The present invention is directed towards a method of preparing quaternary fatty ammonium polyalkoxylates having two symmetrical or nearly symmetrical alkoxylate chains in a one-pot alkoxylation reaction, the products obtained using this method, surfactant compositions comprising these products and their uses.

Background

Quaternary, alkoxylated fatty ammonium compounds belong to the class of cationic surfactants and are widely used for various applications, including fabric softening (see US 5,574,179, US 6,004,913), shampoos and hair conditioning (US 4,744,977, US 6,322,778, US 7,951,762), surface cleaners, e.g. household, car, etc. (US 6,268,324, US 6,821,943 EP 2 240 561B1), cosmetics (US 6,919,074, US 7,074,395), oral care (US 7,534,816), antimicrobial handsoaps or cleaners (US 6,010,991, US 2004/0071653), oilfield applications (US 7,422,064, US 7,776,798), anti corrosion applications as well as agricultural uses, such as herbicidal activity in pesticides (US 201 1/0015071, US 2010/0016163).

There are various methods of production to obtain quaternary alkoxylated fatty ammonium compounds. Typically, alkoxylation of a (primary or secondary) fatty amine is performed under aqueous conditions using acidic or basic catalysis to obtain the corresponding fatty amine alkoxylate. Subsequent quaternization is typically carried out using known quaternizing agents, such as dimethyl sulfate, methyl chloride, benzyl chloride, ethylene oxide and the like, give the desired quaternary fatty ammonium alkoxylate. Yet, these commonly used methods of production still suffer from drawbacks: First, products obtained by current methods typically represent a polydisperse mixture of polyalkoxylates having a random length chain distribution (e.g. characterized by a Poisson distribution). Thus there is a lack of control during the alkoxylation reaction, such that a well-defined, narrow distribution of polyalkoxy substituents is difficult to achieve. Yet, it is known, that length and distribution of the polyalkoxylate chains of fatty amine compounds is critical to their performance in the intended application. Second, the overall efficiency of the reaction is affected by the generation of various side products (often in not insignificant amounts), most prominently dioxane, dioxolane and polymerized products such as PEGs, which not only necessitates work

up procedures to obtain clean products, but also may be hazardous to the environment. Thus, the ability to produce fatty ammonium polyalkoxylates in a selective and controlled manner having (nearly) symmetrical (which refers to symmetrical and nearly symmetrical) alkoxy substituents, while reducing the amount of side products to a minimum is crucial. During the past decade, efforts to improve production methods included varying reaction parameters, such as temperature, pressure, feeding rates and molar ratios of reactants, use and nature of various catalysts (to tune the reactivity of the reactants), as well as mechanical parameters, such as reactor design, mixing properties, and the like. Yet, there is still a need for a production method to allow close control of the structural composition of the final product and to achieve minimal production of any side products, yet is also cost efficient and characterized by ease of handling.

Applicants have now discovered a method to produce quaternary fatty ammonium polyalkoxylates of well defined and predictable structure, and thus allows to overcome the above problems associated with the prior art methods. The method of the invention comprises a unique series of alkoxylation steps performed in a one pot reaction, which allows rigorous control of the degree of alkoxylation and thus the chain length distribution of the obtained quaternary fatty ammonium polyalkoxylates, while eliminating production of wasteful and hazardous side products. In particular, the method of the invention includes a three-step alkoxylation reaction which is performed under strict anhydrous conditions in a one-pot reaction and thus without the need for isolating and/or purifying intermediate products. The final quaternary fatty ammonium polyalkoxylates are characterized by a controlled structural composition having a symmetrical or nearly symmetrical distribution of long-chain alkoxylate substituents, i.e. through symmetrical extension the polyalkoxylates have two alkoxylate chains of equal length. The polyalkoxylates of the invention are thus of high purity and there is no need for any further purification.

Summary of the Invention

In a first aspect the present invention is directed towards a method for preparing a quaternary fatty ammonium polyalkoxylate having two symmetrical or nearly symmetrical alkoxylate chains (i.e. having two alkoxylate chains of equal length) in a one-pot reaction comprising the steps of (a) providing a fatty amine, (b) adding 2 to 4 Mol equivalents of a first alkylene oxide under anhydrous conditions and allowing alkoxylation to occur to obtain a symmetrical tertiary fatty amine N,N-alkoxylate, (c) adding at least 4 Mol equivalents, preferably 4 to 60 Mol equivalents of a second alkylene oxide under anhydrous conditions in the presence of a

basic catalyst and allowing chain extension (of the symmetrical tertiary fatty amine N,N-alkoxylate obtained in step (b)) to occur to obtain a symmetrical tertiary fatty amine N,N-polyalkoxylate, (d) lowering the pH of the reaction mixture obtained in step (c) to a pH of 7 or less, preferably a pH of 2 to 4, and (e) adding 1 to 2 Mol equivalents of a third alkylene oxide to obtain the quaternary fatty ammonium polyalkoxylate.

More specifically, the quaternary fatty ammonium polyalkoxylate having 2 symmetrical alkoxylate chains is a quaternary fatty ammonium polyalkoxylate of formula I $[R_1R_2R_3N^+$-CHR_e-CHR_f-O-$(CHR_e$-CHR_f-$O)_pH]$ X^-, wherein

R_1 is a linear or branched, saturated or unsaturated, aliphatic or aromatic, substituted or unsubstituted C(6-24) hydrocarbon radical or a mixture thereof,

R_2 is a group of formula -CHR_a-CHR_b-O-$(CHR_a$-CHR_b-$O)_nH$ and R_3 is a group of formula -CHR_c-CHR_d-O-$(CHR_c$-CHR_d-$O)_mH$,

n and m are an integer of from 4 to 60, e.g. 4 to 40, preferably 4 to 20, more preferably 5 to 15, most preferably 5 to 10, with the proviso that n and m are either the same integer or integers differing by 1 or 2,

R_a, R_b, R_c, R_d, R_e, R_f are independently of each other H or Me,

p is 0 or 1, and

X^- is a counterion selected from the group consisting of species generated from a mineral acid or organic acid,

in a one-pot reaction comprising the steps of:

(a) providing a fatty amine of formula R_1-NH_2, wherein R_1 is as defined above,

(b) adding 2 to 4 Mol equivalents of a first alkylene oxide under anhydrous conditions and allowing alkoxylation to occur to obtain a tertiary fatty amine N,N-alkoxylate of formula II $R_1R_2R_3N$, wherein R_1 is as defined above, R_2 is a group of formula -CHR_a-CHR_b-O-$(CHR_a$-CHR_b-$O)_nH$ and R_3 is a group of formula -CHR_c-CHR_d-O-$(CHR_c$-CHR_d-$O)_mH$, groups R_a, R_b, R_c, R_d are as defined above, and n and m are the same and an integer selected from 0, 1 or 2,

(c) adding at least 4 Mol equivalents, preferably 4 to 60 Mol equivalents of a second alkylene oxide under anhydrous conditions in the presence of a basic catalyst and allowing chain extension (of the tertiary fatty amine N,N-alkoxylate obtained in step (b)) to occur to obtain a tertiary fatty amine N,N-polyalkoxylate of formula III $R_1R_2R_3N$, wherein R_1 is as defined

above, R_2 is a group of formula $-CHR_a-CHR_b-O-(CHR_a-CHR_b-O)_nH$ and R_3 is a group of formula $-CHR_c-CHR_d-O-(CHR_c-CHR_d-O)_mH$, groups R_a, R_b, R_c, R_d are as defined above, and n and m are an integer of from 4 to 60, e.g. 4 to 40, preferably 4 to 20, more preferably 5 to 15, most preferably 5 to 10, with the proviso that n and m are either the same integer or integers differing by 1 or 2,

(d) lowering the pH of the reaction mixture obtained in step (c) to a pH of 7 or less, preferably a pH of 2 to 4, and

(e) adding 1 to 2 Mol equivalents of a third alkylene oxide to obtain the quaternary fatty ammonium polyalkoxylate of formula I $[R_1R_2R_3N^+-CHR_e-CHR_f-O-(CHR_e-CHR_f-O)_pH]X^-$ as defined above.

In preferred embodiments the first and second and third alkylene oxide are independently of each other EO or PO, more preferably EO, and R_a, R_b, R_c, R_d, R_e, R_f are H.

In other preferred embodiments, the fatty amine is a (C6-24)alkyl- or (C6-24)alkenylamine, preferably oleylamine.

Typical embodiments of the various steps of the present methods include that the fatty amine in step (a) is dried in vacuo at a temperature of from 40° to 140°C, preferably 80° to 140°C, prior to subjecting it to step (b), that step (b) is performed at a pressure of 2.5 bar or less, that the basic catalyst in step (c) is selected from alkaline salts and alkali metal alkoxylates such as NaH, NaOH, NaOEt, NaOMe, KH, KOH, KOtBu, KOEt, CaO, CaH, $Ca(OH)_2$,$Ca(OCH(CH_3)_2)_2$, preferably NaOH and KOH, and that the mineral acid or organic acid used in step (d) are preferably selected from hydrochloric acid, phosphoric acid, sulfuric acid, formic acid, acetic acid, 2-ethylhexanoic acid, lactic acid.

In a further aspect the present invention includes quaternary fatty ammonium polyalkoxylates of formula $[R_1R_2R_3N^+-CHR_e-CHR_f-O-(CHR_e-CHR_f-O)_pH]\ X^-$ obtained according to a method of the invention, which distinguish themselves from the prior art by the designed symmetry of the alkoxylate chains R_2 and R_3, as well as compositions comprising a quaternary fatty ammonium polyalkoxylate of formula $[R_1R_2R_3N^+-CHR_e-CHR_f-O-(CHR_e-CHR_f-O)_pH]\ X^-$ as obtained according to a method of the invention optionally with at least one further component or additive.

In yet a further aspect the present invention also includes a surfactant composition comprising one or more quaternary fatty ammonium polyalkoxylates having two symmetrical alkoxylate

chains (i.e. having two alkoxylate chains of equal length), preferably a surfactant composition, wherein the one or more quaternary fatty ammonium polyalkoxylates are of formula I $[R_1R_2R_3N^+\text{-}CHR_e\text{-}CHR_f\text{-}O\text{-}(CHR_e\text{-}CHR_f\text{-}O)_pH]\ X^-$, wherein R_1 is a linear or branched, saturated or unsaturated, aliphatic or aromatic, substituted or unsubstituted C(6-24) hydrocarbon radical or a mixture thereof, R_2 is a group of formula $-CHR_a\text{-}CHR_b\text{-}O\text{-}(CHR_a\text{-}CHR_b\text{-}O)_nH$ and R_3 is a group of formula $-CHR_c\text{-}CHR_d\text{-}O\text{-}(CHR_c\text{-}CHR_d\text{-}O)_mH$, n and m are an integer of from 4 to 60, e.g. 4 to 40, preferably 4 to 20, more preferably 5 to 15, most preferably 5 to 10, with the proviso that n and m are either the same integer or integers differing by 1 or 2, groups R_a, R_b, R_c, R_d are independently of each other H or Me, p is 0 or 1, and X^- is a counterion selected from the group consisting of species generated from a mineral acid or organic acid.

In yet another aspect the present invention also includes the use of a quaternary fatty ammonium polyalkoxylate of formula $[R_1R_2R_3N^+\text{-}CHR_e\text{-}CHR_f\text{-}O\text{-}(CHR_e\text{-}CHR_f\text{-}O)_pH]\ X^-$ as obtained according to a method of the invention as softeners in fabric care, in personal care products, as deposit dispersants, and in agrochemical formulations.

Brief Description of the Figures

Figure 1. Structure of an exemplary quaternary, nearly symmetrical POE (8-10) C(9-22) fatty ammonium polyalkoxylate.

Figure 2: ^{13}C NMR of quaternized oleylamine of Example 1 (A) and comparative tertiary product (B).

Detailed Description

It is an object of this invention to provide a method of preparing quaternary fatty ammonium polyalkoxylates having two symmetrical or nearly symmetrical alkoxylate chains in a one-pot reaction under anhydrous conditions (also called method of the invention), i.e. having two alkoxylate chains of equal length. A representative structure is shown in Figure 1.

More specifically, the methods comprise the steps of (i) alkoxylating a primary fatty amine under anhydrous conditions in the absence of a catalyst using a suitable alkoxylation agent to obtain a symmetrical tertiary fatty amine N,N-alkoxylate, (ii) extending the N,N-alkoxylate groups by reacting the tertiary fatty amine N,N-alkoxylate with a suitable alkoxylation agent in the presence of a basic catalyst (under controlled temperature and pressure conditions) to obtain a symmetrical tertiary fatty amine N,N-polyalkoxylate, and (iii) reacting the

symmetrical tertiary fatty amine N,N-polyalkoxylate with a suitable alkoxylation agent under neutral to acidic conditions to obtain the desired quaternary fatty ammonium polyalkoxylate.

Thus, in one embodiment, the present invention is directed towards a method of preparing quaternary fatty ammonium polyalkoxylates having 2 symmetrical alkoxylate chains in a one-pot reaction under anhydrous conditions comprising the steps of:

(a) providing a fatty amine,

(b) adding 2 to 4 Mol equivalents of a first alkylene oxide under anhydrous conditions (and in the absence of a catalyst) and allowing alkoxylation to occur to obtain a symmetrical tertiary fatty amine N,N-alkoxylate,

(c) adding at least 4 Mol equivalents, preferably 4 to 60 Mol equivalents, of a second alkylene oxide under anhydrous conditions in the presence of a basic catalyst and allowing chain extension (of the symmetrical tertiary fatty amine N,N-alkoxylate obtained in step (b)) to occur to obtain a symmetrical tertiary fatty amine N,N-polyalkoxylate,

(d) lowering the pH of the reaction mixture obtained in step (c) to a pH of 7 or less, preferably a pH of 2 to 4, and

(e) adding 1 to 2 Mol equivalents of a third alkylene oxide to obtain the quaternary fatty ammonium polyalkoxylate.

The obtained product may be used in situ or stored without any further purification.

In one embodiment, the quaternary fatty ammonium polyalkoxylate having 2 symmetrical alkoxylate chains has the formula I

$[R_1R_2R_3N^+\text{-}CHR_e\text{-}CHR_f\text{-}O\text{-}(CHR_e\text{-}CHR_f\text{-}O)_pH]\ X^-$, wherein

R_1 is a linear or branched, saturated or unsaturated, aliphatic or aromatic, substituted or unsubstituted C(6-24) hydrocarbon radical or a mixture thereof,

R_2 is a group of formula $-CHR_a\text{-}CHR_b\text{-}O\text{-}(CHR_a\text{-}CHR_b\text{-}O)_nH$ and R_3 is a group of formula $-CHR_c\text{-}CHR_d\text{-}O\text{-}(CHR_c\text{-}CHR_d\text{-}O)_mH$,

n and m are 4 to 60, e.g. 4 to 40, preferably 4 to 20, more preferably 5 to 15, most preferably 5 to 10, with the proviso that n and m are either the same integer or integers differing by 1 or 2,

R_a, R_b, R_c, R_d, R_e, R_f are independently of each other H or Me,

p is 0, 1, 2, 3 or 4, preferably 0 or 1, and

X^- is a counterion selected from the group consisting of species generated from a mineral acid or organic acid, preferably a mineral acid.

Preferably groups R_a, R_b, R_c, R_d, R_e, R_f are H.

As used herein the term "symmetrical" in context with the quaternary fatty ammonium polyalkoxylates of the invention (i.e. the wording "having symmetrical or nearly symmetrical alkoxylate chains") indicates that the alkoxylation methods of the invention are performed under rigorous control of the degree of alkoxylation such that the alkoxylate chain substituents R_2 and R_3 of the tertiary fatty amine alkoxylate compounds obtained in steps (b) and (c) are symmetrically extended, i.e. the alkoxylate chains are of equal length. It is understood that the alkoxylate chains may be differing by one or two monomer units and thus may be fully or nearly symmetrical. Therefore, groups n and m (of groups R_2 and R_3) of the quaternary fatty ammonium polyalkoxylates of formula $[R_1R_2R_3N^+\text{-}CHR_e\text{-}CHR_f\text{-}O\text{-}(CHR_e\text{-}CHR_f\text{-}O)_pH]\ X^-$ as defined herein are the same, i.e. n and m are either the same integer (in the case of symmetrical alkoxylate chains) or integers differing by 1 or 2 (in the case of nearly symmetrical alkoxylate chains). Thus, the selective and controlled alkoxylation of fatty amines allows to design and produce quaternary fatty ammonium polyalkoxylates of a specific structural composition (and thus specific properties), which is different from the known compounds of the art, which typically show a Gauss distribution of different grades of alkoxylation. Such a quaternary fatty ammonium polyalkoxylate of the invention having two symmetrical ethoxylate chains is herein also designated POE (4-60) C(6-24) fatty ammonium polyalkoxylate of the invention (i.e. with POE (4-60) indicating that the length of the two polyoxyethyelene (POE) chains is an integer from 4 to 60 and C(6-24) defining the hydrocarbon chain length of the fatty amine to be an integer from 6 to 24). For convenience, the compounds of the invention are hereinafter referred to as being symmetrical, which includes the term "nearly symmetrical".

In one embodiment, the symmetrical tertiary fatty amine N,N-alkoxylate obtained in step (b) is a compound of formula II $R_1R_2R_3N$, wherein

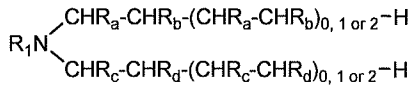
R_1 is a linear or branched, saturated or unsaturated, aliphatic or aromatic, substituted or unsubstituted C(6-24) hydrocarbon radical or a mixture thereof,

R_2 is a group of formula $\text{-}CHR_a\text{-}CHR_b\text{-}O\text{-}(CHR_a\text{-}CHR_b\text{-}O)_nH$ and R_3 is a group of formula $\text{-}CHR_c\text{-}CHR_d\text{-}O\text{-}(CHR_c\text{-}CHR_d\text{-}O)_mH$,

n and m are an integer selected from 0, 1 or 2, preferably 0 or 1,

R_a, R_b, R_c, R_d are independently of each other H or Me.

A compound of formula II may be represented by the following structural formula:



Preferably, R_a, R_b, R_c, R_d are H.

In a further embodiment, the symmetrical tertiary fatty amine N,N-polyalkoxylate obtained in step (c) is a compound of formula III $R_1R_2R_3N$, wherein

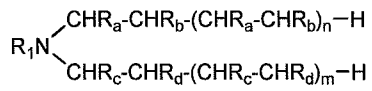
R_1 is a linear or branched, saturated or unsaturated, aliphatic or aromatic, substituted or unsubstituted C(6-24) hydrocarbon radical or a mixture thereof,

R_2 is a group of formula $-CHR_a-CHR_b-O-(CHR_a-CHR_b-O)_nH$, and R_3 is a group of formula $-CHR_c-CHR_d-O-(CHR_c-CHR_d-O)_mH$,

n and m are an integer of from 4 to 60, e.g. 4 to 40, preferably 4 to 20, more preferably 5 to 15, most preferably 5 to 10, with the proviso that n and m are either the same integer or integers differing by 1 or 2,

R_a, R_b, R_c, R_d are independently of each other H or Me.

A compound of formula III may be represented by the following structural formula:



Preferably, R_a, R_b, R_c, R_d are H.

The obtained product may be used in situ or stored without any further purification.

The term "one-pot" reaction as used herein refers to a reaction comprising a series of steps that may be performed in a single reaction vessel. One-pot procedures are particularly desirable as they eliminate the need for isolation (e.g., purification) of intermediates while typically reducing the production of waste materials (e.g., solvents, impurities, side reaction products). Other advantages include ease of handling and typically reduction of overall reaction time.

As used herein, the term "anhydrous" refers to a water content of less than 1%, in particular less than 0.1%, preferably less than 0.05%, but does not exclude the possibility of the presence of some minor amounts of water arising from the reaction itself, such as water of crystallization arising from the catalyst.

The term "alkylene oxide" refers to (C_1-C_6)alkyl oxiranes such as ethylene oxide (EO), propylene oxide (PO) and butylene oxide (BO), preferably EO and PO, more preferably EO. The term "alkoxylated" as used herein in combination with fatty amine refers to the product obtained when a fatty amine has been reacted with at least one alkylene oxide, resulting in a fatty amine carrying as a substituent the corresponding ring opened reaction product of the at least one alkylene oxide. The alkylene oxide-substituent may consist of one or more alkylene oxide units that are linked via ether bonds. The first, second and third alkylene oxide used in steps (b), (c) and (e) may be the same or different, preferably they are the same, more preferably they are EO.

Typically, m and n in compounds of formula I or III are an integer of from 4 to 60, e.g. 4 to 40, preferably 5 to 15, more preferably 5 to 10, most preferably about 8. It is understood, that the symmetry of the two alkoxylate chains indicates that m and n are either the same integer or integers differing by 1 or 2.

The fatty amines that are used in the present methods as starting material are not limited and may be any one of animal based oils and fats derived from beef tallow, fish oil, lanolin, etc.; plant based oils and fats derived from coconut oil, palmoil, soybeanoil, etc.; synthetic fatty acid alkyl esters derived from α-olefins by means of using an oxo-synthesis method.

More specifically, the fatty amine is a primary amine of the formula R_1-NH_2, wherein R_1 is a linear or branched, saturated or unsaturated, aliphatic or aromatic, substituted or unsubstituted C(6-24) hydrocarbon radical or a mixture of different linear or branched, saturated or unsaturated, aliphatic or aromatic, substituted or unsubstituted C(6-24) hydrocarbon radicals. The term "saturated" as used herein refers to an alkyl fatty amine, which is a hydrocarbon radical having a fully saturated aliphatic or alicyclic backbone, i.e., with no double bonds. The term "unsaturated" as used herein refers to "the state in which not all of the available valence bonds along an alkyl chain are satisfied" (Hawley's Condensed Chemical Dictionary, 1151, 14th Edition, 2002, by John Wiley & Sons, Inc.). More specifically, the term "unsaturated" in reference to a fatty amine refers to an alkenyl fatty amine, which is a hydrocarbon radical having at least one double bond, preferably 1 to 3 double bonds in the hydrocarbon chain R_1. The term "substituted" in reference to a fatty amine refers to substitution of the hydrocarbon chain R_1 by groups selected from hydroxy, oxo, carboxyl, amino, C1-C6-alkyl, C1-C6-alkenyl and C1-C6-alkoxyhydroxyl, and the like. Preferably, the fatty amines are unsubstituted.

In a specific embodiment, R_1 is a linear or branched, saturated or unsaturated, aliphatic or aromatic hydrocarbon radical having from 6 to 24 carbon atoms, preferably 12 to 24 carbon atoms, more preferably 12 to 20 carbon atoms. Illustrative examples of suitable alkyl- or alkenyl-fatty groups of the fatty amines for use as starting materials in the methods of the invention include, but are not limited to, hexyl, heptyl, n-octyl, p-tert. octyl, n-nonyl-, p-tert. nonyl, decyl, lauryl, tridecyl, myristyl, palmityl, stearyl, arachidyl, hydroabietyl or behenyl, 2-ethylhexyl, 2-propylheptyl, linolenyl, stearidonyl, linoleyl, arachidonyl, palmitoleyl, oleyl, elaidyl, tallow alkyl, hydrogenated tallow alkyl, rape seed alkyl, soya alkyl, coco alkyl and the like. The term "fatty amine" also includes commercially available fatty amines such as Armeen® amines (available from Akzo Chemicals, Chicago, III.) such as Akzo's Armeen C, Armeen O, Armeen OL, Armeen T, Armeen HT, Armeen S and Armeen SD, wherein the letter designation relates to the fatty group, such as coco, oleyl, tallow, or stearyl groups, or Genamin® amines (available from Clariant) having e.g. stearyl, tallow fat or oleyl moieties. Suitable fatty amines can also be prepared from corresponding fatty acids or fatty alcohols according to methods well known in the art of organic synthesis. Thus, any amines derived from other specifically recited fatty alcohols and fatty acids are contemplated as well. Combinations of two or more fatty amines, and combinations of one or more fatty amines and one or more other lipid compounds also are contemplated. It is understood that fatty amines comprising one or more double bonds may exist as cis- or trans-isomer or mixtures thereof. The skilled person will understand that unless stated specifically all isomeric structures (in pure form or as mixtures) are contemplated herein. Unless stated otherwise, structures as shown herein are only representative for all isomers. Likewise, if charges in quaternary products and/or counterions are not shown, it is understood that these are included and the skilled person will be able to derive it from the application as a whole.

Preferably, the fatty amine used as starting material is dried in vacuo at elevated temperatures. Thus, the term “under anhydrous conditions” includes drying the starting fatty amine to a water content of less than 1%, in particular less than 0.1%, preferably less than 0.05%, which is typically achieved by drying in vacuo at a temperature of from 40° to 140°C, preferably 80° to 140°C, for at least 15 minutes, preferably between 15 to 90 minutes before subjecting it to an alkoxylation reaction according to step (b).

In one embodiment, step (b) is performed by adding the alkylene oxide gradually to the dried fatty amine (to control the exothermicity and pressure build-up of the reaction). In another embodiment, step (b) is conducted at a pressure of 2.5 bar or less to control production of potential side products, preferably at a pressure between 1.0 and 2.5 bar.

In other embodiments, the temperature of the alkoxylation steps, i.e. during addition of the first, second and third alkylene oxide, is typically less than 150°C, such as 100 to 150°C, preferably 120 to 150°C. The addition of the basic catalyst and the neutralization step with the mineral or organic acid is typically performed at 60 to 80°C.

In further embodiments, alkoxylation in step (c) is performed using a basic catalyst. As used herein, the term "basic catalyst" includes any catalysts which are basic or alkaline, preferably a basic salt of the alkali metals of Group I of the Periodic Table, e.g., sodium, potassium, rubidium, and cesium, or a basic salt of certain alkaline earth metals of Group II of the Periodic Table, e.g., calcium, strontium, barium, magnesium. Typical basic catalysts include alkaline salts and alkali metal alkoxylates such as NaH, NaOH, NaOEt, NaOMe, KH, KOH, KOtBu, KOEt, CaO, CaH, $Ca(OH)_2$,$Ca(OCH(CH_3)_2)_2$, and mixtures thereof. Preferably, the basic catalyst used in step (c) is KOH or NaOH,

The catalysts may be employed at concentrations of about 0.01 wt% to about 1.5 wt%, preferably about 0.01 wt% to about 1.0 wt%, more preferably about 0.05 wt% to about 0.5 wt%, most preferably about 0.05 wt% to about 0.25 wt%, typically about 0.1 wt% based on the amount of fatty amine used.

Typically, step (c) is carried out by first adding the basic catalyst, preferably at ambient temperature, and subsequently adding the second alkylene oxide, preferably at elevated temperatures.

In other specific embodiments the pH in step (d) is lowered by using a mineral acid or organic acid, preferably a mineral acid. As used herein the term “mineral acid” refers to hydrochloric acid, hydrobromic acid, nitric acid, phosphoric acid, sulfuric acid, boric acid, hydrofluoric acid, perchloric acid, and the like, preferably hydrochloric acid, phosphoric acid, sulfuric acid, more preferably hydrochloric acid. The term “organic acid” includes, but is not limited to, formic acid, acetic acid, propionic acid, butyric or isobutyric acid, 2-ethylhexanoic acid, mono- or di- or trichloroacetic acid, mono- or di- or trifluoroacetic acid, α- or β- or γ-chlorobutyric acid, lactic acid, glycolic acid, pyruvic acid, glyoxalic acid, acrylic acid and like monocarboxylic acids, methanesulfonic acid, toluenesulfonic acid and like sulfonic acids, oxalic acid, succinic acid, adipic acid, tartaric acid, citric acid and like polycarboxylic acids, preferably formic, acid acetic acid, lactic acid, 2-ethylhexanoic acid.

The mineral acid or organic acid of choice may be used in an amount of less than 5 wt%, preferably less than 3 wt%, more preferably less than 2 wt%. In preferred embodiments the

mineral acid may be used from 0.01 to 5 wt%, more preferably from 0.01 to 3 wt%, most preferably from 0.1 to 2 wt%, based on the amount of catalyst used.

Thus, in a specific embodiment, the present invention is directed towards a method for preparing a quaternary fatty ammonium polyalkoxylate of formula I $[R_1R_2R_3N^+\text{-}CHR_e\text{-}CHR_f\text{-}O\text{-}(CHR_e\text{-}CHR_f\text{-}O)_pH]\ X^-$ having 2 symmetrical alkoxylate chains, wherein

R_1 is a linear or branched, saturated or unsaturated, aliphatic or aromatic, substituted or unsubstituted C(6-24) hydrocarbon radical or a mixture thereof,

R_2 is a group of formula $-CHR_a\text{-}CHR_b\text{-}O\text{-}(CHR_a\text{-}CHR_b\text{-}O)_nH$ and R_3 is a group of formula $-CHR_c\text{-}CHR_d\text{-}O\text{-}(CHR_c\text{-}CHR_d\text{-}O)_mH$,

n and m are an integer of from 4 to 60, e.g. 4 to 40, preferably 4 to 20, more preferably 5 to 15, most preferably 5 to 10, with the proviso that n and m are either the same integer or integers differing by 1 or 2,

R_a, R_b, R_c, R_d, R_e, R_f are independently of each other H or Me,

p is 0 or 1, and

X^- is a counterion selected from the group consisting of species generated from a mineral acid or organic acid,

in a one-pot reaction comprising the steps of:

(a) providing a fatty amine of formula $R_1\text{-}NH_2$, wherein R_1 is as defined above,

(b) adding 2 to 4 Mol equivalents of a first alkylene oxide, which is selected from EO or PO, preferably EO, under anhydrous conditions (and in the absence of a catalyst) and allowing alkoxylation to occur to obtain a tertiary fatty amine N,N-alkoxylate of formula II $R_1R_2R_3N$, wherein R_1 is as defined above, R_2 is a group of formula $-CHR_a\text{-}CHR_b\text{-}O\text{-}(CHR_a\text{-}CHR_b\text{-}O)_nH$ and R_3 is a group of formula $-CHR_c\text{-}CHR_d\text{-}O\text{-}(CHR_c\text{-}CHR_d\text{-}O)_mH$, groups R_a, R_b, R_c, R_d are as defined above, and n and m are the same and are an integer selected from 0, 1 or 2,

(c) adding at least 4 Mol equivalents, preferably 4 to 60 Mol equivalents of a second alkylene oxide, which is selected from EO or PO, preferably EO, under anhydrous conditions in the presence of a basic catalyst and allowing chain extension (of the tertiary fatty amine N,N-alkoxylate obtained in step (b)) to occur to obtain a tertiary fatty amine N,N-polyalkoxylate of formula III $R_1R_2R_3N$, wherein R_1 is as defined above, R_2 is a group of

formula -CHR_a-CHR_b-O-(CHR_a-CHR_b-O)$_n$H and R_3 is a group of formula -CHR_c-CHR_d-O-(CHR_c-CHR_d-O)$_m$H, groups R_a, R_b, R_c, R_d are as defined above, and n and m are an integer of from 4 to 60, e.g. 4 to 40, preferably 4 to 20, more preferably 5 to 15, most preferably 5 to 10, with the proviso that n and m are either the same integer or integers differing by 1 or 2,

(d) lowering the pH of the reaction mixture obtained in step (c) to a pH of 7 or less, preferably a pH of 2 to 4, and

(e) adding 1 to 2 Mol equivalents of a third alkylene oxide, which is selected from EO or PO, preferably EO, to obtain the quaternary fatty ammonium polyalkoxylate of formula I $[R_1R_2R_3N^+$-CHR_e-CHR_f-O-(CHR_e-CHR_f-O)$_p$H] X^- as defined above.

After addition of the alkylene oxide the reaction mixture is subjected to an afterstirring time of typically up to 4 hours, preferably 0.5 to 2 hours, more preferably 1 hour, to allow for full conversion and complete reduction of pressure, thereby avoiding the formation of PEG sideproducts.

The quaternary fatty ammonium polyalkoxylates obtained by the methods of the invention are characterized by a well-defined structural composition, which is indicated by having 2 symmetrical alkoxylate chains, and thus can be distinguished from corresponding polyalkoxylated compounds of the prior art, which typically show a statistical distribution of polyalkoxylate chains. This was achieved by dividing the alkoxylation reaction into three steps (b), (c), and (e): the first alkoxylation of step (b) replaces the two acidic H atoms in a symmetrical way by one or two hydroxyalkyl units under anhydrous conditions; the second alkoxylation of step (c) allows to extend the hydroxyalkyl units in a symmetrical way in the presence of a basic catalyst under anhydrous conditions; and the third alkoxylation of step (e) is used for selectively quaternizing the tertiary alkoxylated fatty amine, i.e. without obtaining chain extension of the nearly symmetrical alkoxylate chains obtained in the first and second alkoxylation. This separation of alkoxylation reactions and the carefully controlled reaction conditions – albeit still as a one pot procedure – allows close control of the structural composition by appropriate choice of the molar ratio between fatty amine starting material and first, second and third alkoxylation agent, respectively, added in steps (b), (c) and (e) of the methods of the invention.

The quaternary fatty ammonium polyalkoxylates of the invention may be used singly, or in combination with one another to form mixtures and/or in admixture with other components and additives to form compositions suitable for the intended use. Thus, the invention is also

directed towards a surfactant composition comprising quaternary fatty ammonium polyalkoxylates of the invention having two symmetrical alkoxylate chains as defined above. More specifically, typically at least 90%, preferably at least 95%, more preferably at least 98% of the quaternary fatty ammonium polyalkoxylates of the invention have symmetrical alkoxylate chains.

In specific embodiments the surfactant composition of the present invention comprise quaternary fatty ammonium polyalkoxylates with two symmetrical alkoxylate chains of the formula $[R_1R_2R_3N^+\text{-}CHR_e\text{-}CHR_f\text{-}O\text{-}(CHR_e\text{-}CHR_f\text{-}O)_pH]\ X^-$ as defined above, i.e. wherein R_1 is a linear or branched, saturated or unsaturated, aliphatic or aromatic, substituted or unsubstituted C(6-24) hydrocarbon radical or a mixture thereof,

R_2 is a group of formula $\text{-}CHR_a\text{-}CHR_b\text{-}O\text{-}(CHR_a\text{-}CHR_b\text{-}O)_nH$ and R_3 is a group of formula $\text{-}CHR_c\text{-}CHR_d\text{-}O\text{-}(CHR_c\text{-}CHR_d\text{-}O)_mH$,

n and m are an integer of from 4 to 60, e.g. 4 to 40, preferably 4 to 20, more preferably 5 to 15, most preferably 5 to 10, with the proviso that n and m are either the same integer or integers differing by 1 or 2,

R_a, R_b, R_c, R_d, R_e, R_f are independently of each other H or Me,

p is 0 or 1, and

X^- is a counterion selected from the group consisting of species generated from a mineral acid or organic acid.

Typically, the surfactant composition of the invention comprises one or more fatty ammonium polyalkoxylates of the invention having two symmetrical alkoxylate chains in an amount of 0.001 to 99.99 %, preferably 50.0 to 99.99%.

In some embodiments, the surfactant composition of the present invention comprises quaternary fatty ammonium polyalkoxylates with two symmetrical alkoxylate chains of the formula $[R_1R_2R_3N^+\text{-}CHR_e\text{-}CHR_f\text{-}O\text{-}(CHR_e\text{-}CHR_f\text{-}O)_pH]\ X^-$ as defined above, wherein R_a, R_b, R_c, R_d, R_e, R_f are H. In other embodiments the mineral acid is selected from hydrochloric acid, hydrobromic acid, nitric acid, phosphoric acid, sulfuric acid, boric acid, hydrofluoric acid, perchloric acid, and the organic acid is selected from formic acid, acetic acid, 2-ethylhexanoic acid, lactic acid.

Other components that may or may not be present in the surfactant compositions of the invention include, but are not limited to, nonionic, cationic or anionic surfactants (in amounts

typically used for the intended application). Optional additives include, but are not limited to, pH adjusting agents and pH buffers including organic and inorganic salts; non-aqueous solvents, perfumes, perfume carriers, optical brighteners, coloring agents such as dyes and pigments, opacifying agents, hydrotropes, antifoaming agents, viscosity modifying agents such as thickeners, enzymes, anti-spotting agents, anti-oxidants, anti-corrosion agents as well as others not specifically elucidated here. For applications as a deposit dispersant the quaternary fatty ammonium polyalkoxylates of the invention may be used in combination with a biocidal agent, such as dodecylguanidine hydrochloride; methylene bis (thiocyanate); n-alkyl dimethylbenzylammonium chloride; glutaraldehyde; 2,2-dibromo-3-nitrilo propionamide; 5-chloro-2-methyl-4-isothiazolin-3-one; 2-methyl-4-isothiazolin-3-one; or 2-bromo-2-nitropropane-l,3-diol; sodium or calcium hypochlorite; sodium bromide; β-bromo-β-nitrostyrene; oxazolidines; chromated copper arsenate; zinc pyrithione; copper pyrithione; a carbamate; a halohydantoin; dinonylsulfosuccinate; sodium dioctylsulfosuccinate (SDSS), disodium lauryl sulfosuccinate, sodium lauryl sulfoacetate, and the like.

The final compositions comprising one or more compounds obtained according to the present methods of the invention may be aqueous or nonaqueous (depending on the intended application).

In a further aspect, the present invention is also directed towards uses of the polyalkoxylates of the invention (or compositions thereof) in various applications and endproducts. They may be used as softeners, for example in detergent formulations, such as liquid and powdered laundry detergents, liquid and sheet fabric softeners. Thus, the present invention also contemplates detergent formulations comprising a compound of the invention.

A further application includes their use in personal care products such as liquid cleansing products, conditioning bars, oral care products, hair care products, cosmetics, and the like. Thus, the present invention also contemplates personal care products comprising a compound of the invention.

Yet another application is their use as deposit dispersant. For example, the compounds of the invention are particularly efficient in deposit control applications, especially in preventing (or removing) organic or inorganic attachment to surfaces of any article and subsequent biofilm formation and any corrosion effects, which may be found in various environments including biological, medical, commercial (textiles), industrial (food, paper, transport industries, construction, metal, chemical, oil and gas, power, petrochemical), and other processing operations. Their use may be for example in hard and soft surface detergents, sanitizers and

disinfectants, especially for cleaning surfaces contaminated with e.g. of gram positive and/or gram negative bacteria. Surfaces to be treated include (i) soft surfaces having a softer, highly flexible material such as fabric, carpet, leather, paper, wood, rubber, hair, and skin, and (ii) hard surfaces such as glazed and unglazed tile, porcelain, ceramics as well as stone including marble, granite, concrete, and other stones surfaces; composite materials, glass; metals and metal alloys; synthetic or natural polymers, such as plastics e.g. PE (polyethylene), PP (polypropylene), PA (polyamides), PVC (polyvinylchloride), polyester, vinyl; fiberglass, Formica, Corian and other hard surfaces known to the industry. Specific nonlimiting examples of such surfaces can be found in e.g. water handling/processing industries and include plumbing, tubing, and support components involved with water handling, sewerage discharges, paper pulping operations, re-circulating water systems (such as air conditioning systems, a cooling water systems, and the like), and in other water bearing, handling, processing, and collection systems. Other surfaces that have contacts with water may be found in household environment and include in particular surfaces found in washrooms (e.g. shower stalls, bathtubs and bathing appliances, toilets, bidets, drains, wall and flooring surfaces and the like), in kitchens (e.g. cabinets and countertop surfaces, walls and floor surfaces), etc. Other industries or environments where surfaces may be found include e.g. industrial food or beverage production facilities, in paper processing and paper mills, in transport industries (car, boat, train,etc), in piers, oil platforms, pipelines, mining or powerplants (chemical industry, oil and gas recovery, fracking as well). Thus, the present invention also contemplates deposit control formulations comprising a compound of the invention.

Yet a further application is their use in agrochemical formulations. For example, the compounds of the invention may be used as additives in agrochemical formulations to promote penetration of an agrochemically active compound(s) of choice into the plant and thereby enhance the activity of the active compound(s). In one embodiment the compounds of the invention may be able to increase wettability of the formulation and thus lead to a better distribution of the spray coating on the surface of the plant, which will increase the availability of the active compound (which have to penetrate into the plant to be able to unfold their systemic activity evenly throughout the plant). The use of the present compounds in agrochemical formulations will allow to overcome the drawbacks of currently known agrochemical formulations, which typically include surfactants that are environmentally unsafe or toxic, have irritant properties and/or are only minimally biodegradable. Thus the

present invention also contemplates agrochemical formulations comprising at least one agrochemically active compound and at least one compound of the invention.

In one embodiment the agrochemically active compound (also called agrochemical) may be a biocidal compound, i.e. a chemical substance capable of killing or inhibiting growth, division, reproduction, or spread of microorganisms, such as bacteria, algae, and fungi used in the field of agriculture (which includes any type of intensive cultivation of land). Known biocidal compounds include e.g. pesticides, such as for example herbicides, insecticides, fungicides, plant growth regulators, rodenticides, algicides, moluscicides and miticides, as well as antimicrobials, such as for example germicides, antibiotics, antibacterials, antivirals, antifungals, antiprotozoals and antiparasites. Typically used agrochemical formulations may include as agrochemically active ingredient a pesticide, such as glufosinate (salts), glyphosate (salts), paraquat, diquat, dicamba, fomesafen, imazethapyr, imazaquin, imazapyr, propamocarb, clopyralyd and bentazone and the like.

In another embodiment, the agrochemically active compound may be a fertilizer, preferably a partially water-soluble fertilizer, for example a foliar fertilizer, such as urea or foliar macro- or microelement fertilizer, including chelates.

Suitable agrochemical formulations may also include a combination of agrochemically active compounds, such as a combination of herbicides, insecticides and fungicides, and, if desired, fertilizers. Examples of suitable agrochemicals and mixtures of agrochemicals are listed in standard works of reference and will be known to the skilled person.

Typically, an agrochemical formulation is a water-based formulation, preferably in form of a soluble concentrate formulation.

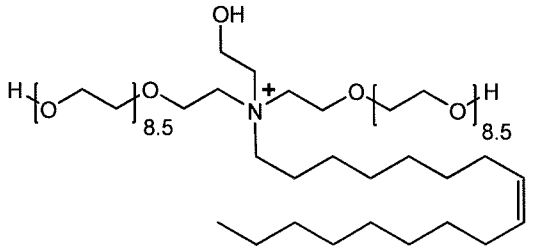
The following examples illustrate the present invention without limiting the invention in any way.

Examples:

Materials and Methods: ^{13}C-NMR spectra were recorded using a 300 MHz UltraShield (Bruker) instrument (respectively 75.5 MHz for ^{13}C) at 300 K. Each sample was prepared by dissolving approx. 170 mg compound in 0.6 ml $CDCl_3$ (Sigma Aldrich) in a 5 mm NMR tube. The standard puls program zgpg30 was used for the ^{13}C-NMR experiments. The conditions were as follows: spectral width 20450 Hz, number of data points 64K, acquisition time 1.6 s, relaxation delay 2.5 s, 10 µs 90° ^{13}C pulse and 2048 scans. The recorded FIDs were processed (Fourier transformation, automatic phase and baseline correction) using TopSpin 2.1

(Bruker). Unless specified otherwise commercially available materials were used (cetylpyridinium chloride monohydrate [CAS No. 6004-24.6] from Merck SDB; Arquad 2HT-75 from Akzo SDB). Advantageous materials for the reactors for use in the methods of the invention are preferably corrosion-resistant Hastelloy® types, glass or ceramic as materials.

Example 1: Preparation of a quaternized (POE 8.5) oleylamine **1**.



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A 2.5L glass autoclave with thermo-jacket (attached to a circulation thermostat) equipped with an overhead stirrer, and thermocouple is charged with 534g distilled oleylamine (e.g. Genamin OL 100D, Clariant MW 267.56, 2 mol). The oleylamine was vacuum dried for approx. 30 minutes at 130°C until water content is below 0.05%. The reactor was heated to about 150°C, and 176g ethylene oxide (MW 44.06 g/mol, 4 mol) was added. After the ethylene oxide has been consumed, stirring was continued for additional 30 minutes whilst cooling down to 90°C. Then the mixture was charged with 2.24g potassium hydroxide (50% aq. solution). Subsequently, the mixture was vacuum dried for approx. 30 minutes at 130°C. The temperature was raised to 150°C and 1320g of ethylene oxide (30 mol) was fed to the reactor. The reaction temperature at this point was 145°C. After the ethylene oxide had been consumed, stirring was continued for additional 30 minutes whilst cooling down to 60°C. Afterwards 231.2g of hydrochloric acid (32%) was added to the mixture to achieve a pH of 3. The mixture was vacuum dried for 1 hour at 130°C until the water content was below 0.05%. Finally, the reactor was heated to 140°C, and 88g of ethylene oxide was added. After the reaction is completed, an afterstirring time of one hour is applied. The final pH of the product (10% in deionised water) was approx. 8.5. The product obtained was a homogeneous, odourless, slightly brownish, clear solution. The yield was approx. 92%. Analysis of structure and purity by ^{13}C-NMR (see Example 3) showed that the total 18 mol of ethylene oxide were distributed symmetrically between the two chain, giving a ratio of alkyleneoxide units of the three substituents of 8.5 : 8.5 : 1. The amine value (which indicates the total amount of amines expressed by the number of milligrams of KOH equivalent to the hydrochloric acid required

to neutralize one gram of a sample) of an aliquot (i.e. prior to quaternization) was ca. 54 mg KOH/g (as determined by standard procedures: DIN Handbook 117, Direction 53176 and 16945, 2nd edition 1984). This is in excellent agreement with the theoretically calculated value of 52 mg KOH/g and confirms the high structural symmetry of the compounds (in contrast to the unsymmetrical prior art compounds. The degree of quaternization was determined by Epton titration (ISO 2271) and yielded 95%.

Example 2: Comparative example of tertiary fatty amine (as described in DE-A-20 52 321):

A 2.5L glass autoclave with thermo-jacket (attached to a circulation thermostat) equipped with an overhead stirrer, and thermocouple is charged with 534g distilled oleylamine (e.g. Genamin OL 100D, Clariant MW 267.56, 2 mol). 36g of deionised water (10 mol) is added. The mixture became viscous whilst stirring. The reactor was evacuated for approx. 30 minutes at room temperature. Upon heating the mixture became fluid again. At 70°C 160g ethylene oxide (MW 44.06 g/mol, 3.6 mol) was added. After additional 120g ethylene oxide the mixture started foaming and became viscous again. Whilst adding additional 200g ethylene oxide at 70°C the foam disappeared and the mixture became highly viscous (stirring stopped sometimes!). Upon addition of further 20g ethylene oxide the product started to foam again. Afterwards, final 1084g of ethylene oxide was added to the product without creating additional foam. However, the mixture became more liquid and turned dark brown. After the ethylene oxide had been consumed, stirring was continued for additional 30 minutes whilst cooling down to 60°C. Afterwards 231.2g of hydrochloric acid (32%) was added to the mixture to achieve a pH of 3. The mixture was vacuum dried for 1 hour at 130°C until the water content was below 0.05%. Finally, the reactor was heated to 140°C, and 88g of ethylene oxide was added. After the reaction was completed, an afterstirring time of one hour was applied. The product obtained was a homogeneous, odourless, dark brownish solution. The yield was approx. 99%. Analysis performed by ^{13}C-NMR (see Example 3) showed that the total 18 mol of ethylene oxide were distributed symmetrically between the two chain, giving a ratio of alkyleneoxide units of the two substituents of 9:9. No evidence was found for a quaternization. The amine value obtained of an aliquot (i.e. prior to the final addition of ethylene oxide to induce quaternization in analogy to Example 1) was ca. 47 mg KOH/g (as determined by standard procedures: DIN Handbook 117, Direction 53176 and 16945, 2nd edition 1984).

Example 3: Characterization

(a) ^{13}C-NMR:

The assignment of the peaks and thus proof of structure was confirmed by comparing ^{13}C-NMR data of the quaternary oleylamine of Example 1 (Figure 2: A) with the tertiary amine of the comparative Example 2 (Figure 2: B). Major differences were observed in the range of 45 to 75 ppm, while aliphatic peaks (0 to 35 ppm) were in agreement for both compounds. As expected, one difference was found for the terminal C-atom of a PEG unit (peaks at 72.6 and 61.5 ppm). The low intensity of these peaks for the compound of Example 1 indicated an equimolar concentration, while the much higher intensity for the tertiary compound indicated a higher concentration. This observed higher concentration was due to formation of PEG (induced by the addition of water). In contrast, any PEG formation was eliminated or reduced to negligible amounts by applying the methods of the present invention. A further difference was the presence of a multitude of signals around the N-atom for the comparative compound (69.6, 55.5, 53.9 and 27.4 ppm), indicating a non-uniform N-environment. In addition, the compound of the present invention showed two additional peaks at 62.6 and 46.2 ppm, which can be attributed to the 2 C-atoms of the ethylene oxide unit introduced in the last step of the method of the invention (quaternization step).

(b) Evaluation of the Aerobic Biodegradability in an Aqueous Medium (Manometric Respirometry Test; (OECD Guidelines for testing chemicals; Test 301F) Stability:

The compound of Example 1 was subjected to the evaluation of the aerobic biodegradability in aqueous media according to OECD 301F. The results are shown in Table 1 in comparison to three reference compounds. The compounds of the invention showed high biodegradability of typically > 60%.

Table 1

Compound/Chemical Name/CAS Nr.	**Biodegradability in % after x days**
Quaternized (POE 8.5) oleylamine **1** (Example 1, Batch 1)	72% after 28 days
Quaternized (POE 8.5) oleylamine **1** (Example 1, Batch 2)	70% after 28 days
Cetylpyridinium chloride monohydrate	25% after 28 days (Merck SDB)
Benzoalkonium chloride	100% after 45 days *
Arquad 2HT-75	68% after 287 days (Akzo SDB)

* Kümmerer K.: Eintrag von Pharmaka, Diagnostika und Desinfektionsmitteln aus Krankenhäusern in die aquatische Umwelt. Habilitationsschrift. Freiburg (1998)

Example 4: Prevention of biofilm formation

The efficacy of quaternized (POE 8.5) oleylamine **1** (of Example 1) to prevent biofilm formation was tested. The product of the invention, a commercially available deposit dispersant of Kolb (mixture of non-ionic surfactants) and a commercially available biocide (didecyldimethylammonium chloride) were tested for their efficiency against the two test germs *Pseudomonas putida* und *Staphylococcus aureus* DSM 799. Biofilms from three bacterial suspension having cell densities of 10^5, 10^6 and 10^7, respectively were cultured and the formation of a biofilm was analysed after 24 and 48 h. A prevention of the formation of a biofilm was initially shown for all three products independent of concentration (10 ppm and 100 ppm).

More specifically, the surface active biocide (didecyldimethylammonium chloride) showed a profound biocidal effect at a concentration of 30 ppm and 100 ppm. It induced a reduction in the live germ count by a factor of 10^5 in the test germs *Pseudomonas aeruginosa* ATCC 15442 (gram negative) and *Staphylococcus aureus* ATCC 6538 (gram positive) within both 30 and 60 minutes. After 24 hours the number of remaining germ colonies had again increased by a factor of 10^4.

In contrast, the product of the invention and the commercially available deposit dispersant did not show any biocidal effect.

Thus, it was shown that compound **1** could effectively and safely prevent biofilm formation of *Pseudomonas putida* in the same range as the two commercially available reference products.

Example 5: Aquatic toxicity

(a) The aquatic toxicity of quaternized (POE 8.5) oleylamine **1** (of Example 1) was tested in a fresh water algal growth inhibition test with Desmodesmus subspicatur (OECD 201; www.oecd.org), wherein the exponentially growing test organism is exposed to the test substance in batch cultures over a period of normally 72 hours. The test endpoint is inhibition of growth, expressed as logarithmic algal biomass increase (average growth rate) during the exposure period. From the average growth rates recorded in a series of test solutions and the concentration bringing about the 50% inhibition of growth is determined and expressed as the nominal median effective concentration EC50. The nominal median effective concentration with respect to growth rate after 72 hours was found to be 3.8 mg/l.

(b) The acute toxicity of quaternized (POE 8.5) oleylamine **1** (of Example 1) was further tested in an acute immobilization test using Daphnia magna (OECD 202; www.oecd.org).

Young daphnids (< 24 hours) are exposed to the test substance at a range of concentrations for a period of 48 hours. Immobilisation is recorded at 24 hours and 48 hours and compared with control values. The results are analysed in order to calculate the EC50 at 48h. The nominal median effective concentration after 48 hours was found to be 5.0 mg/l.

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Claims:

1. A method for preparing a quaternary fatty ammonium polyalkoxylate having 2 symmetrical alkoxylate chains in a one-pot reaction comprising the steps of:

(a) providing a fatty amine,

(b) adding 2 to 4 Mol equivalents of a first alkylene oxide under anhydrous conditions and allowing alkoxylation to occur to obtain a symmetrical tertiary fatty amine N,N-alkoxylate,

(c) adding at least 4 Mol equivalents, preferably 4 to 60 Mol equivalents of a second alkylene oxide under anhydrous conditions in the presence of a basic catalyst and allowing chain extension (of the symmetrical tertiary fatty amine N,N-alkoxylate obtained in step (b)) to occur to obtain a symmetrical tertiary fatty amine N,N-polyalkoxylate,

(d) lowering the pH of the reaction mixture obtained in step (c) to a pH of 7 or less, preferably a pH of 2 to 4, and

(e) adding 1 to 2 Mol equivalents of a third alkylene oxide to obtain the quaternary fatty ammonium polyalkoxylate.

2. A method according to claim 1 for preparing a quaternary fatty ammonium polyalkoxylate of formula I $[R_1R_2R_3N^+\text{-}CHR_e\text{-}CHR_f\text{-}O\text{-}(CHR_e\text{-}CHR_f\text{-}O)_pH]\ X^-$ having 2 symmetrical alkoxylate chains, wherein

R_1 is a linear or branched, saturated or unsaturated, aliphatic or aromatic, substituted or unsubstituted C(6-24) hydrocarbon radical or a mixture thereof,

R_2 is a group of formula $\text{-}CHR_a\text{-}CHR_b\text{-}O\text{-}(CHR_a\text{-}CHR_b\text{-}O)_nH$ and R_3 is a group of formula $\text{-}CHR_c\text{-}CHR_d\text{-}O\text{-}(CHR_c\text{-}CHR_d\text{-}O)_mH$,

n and m are an integer of from 4 to 60, e.g. 4 to 40, preferably 4 to 20, more preferably 5 to 15, most preferably 5 to 10, with the proviso that n and m are either the same integer or integers differing by 1 or 2,

R_a, R_b, R_c, R_d, R_e, R_f are independently of each other H or Me,

p is 0 or 1, and

X^- is a counterion selected from the group consisting of species generated from a mineral acid or organic acid,

in a one-pot reaction comprising the steps of:

(a) providing a fatty amine of formula R_1-NH_2, wherein R_1 is as defined above,

(b) adding 2 to 4 Mol equivalents of a first alkylene oxide under anhydrous conditions and allowing alkoxylation to occur to obtain a tertiary fatty amine N,N-alkoxylate of formula II $R_1R_2R_3N$, wherein R_1 is as defined above, R_2 is a group of formula -CHR_a-CHR_b-O-(CHR_a-CHR_b-O)$_n$H and R_3 is a group of formula -CHR_c-CHR_d-O-(CHR_c-CHR_d-O)$_m$H, groups R_a, R_b, R_c, R_d are as defined above, and n and m are the same and are an integer selected from 0, 1 or 2,

(c) adding at least 4 Mol equivalents, preferably 4 to 60 Mol equivalents of a second alkylene oxide under anhydrous conditions in the presence of a basic catalyst and allowing chain extension (of the tertiary fatty amine N,N-alkoxylate obtained in step (b)) to occur to obtain a tertiary fatty amine N,N-polyalkoxylate of formula III $R_1R_2R_3N$, wherein R_1 is as defined above, R_2 is a group of formula -CHR_a-CHR_b-O-(CHR_a-CHR_b-O)$_n$H and R_3 is a group of formula -CHR_c-CHR_d-O-(CHR_c-CHR_d-O)$_m$H, groups R_a, R_b, R_c, R_d are as defined above and n and m are an integer of from 4 to 60, e.g. 4 to 40, preferably 4 to 20, more preferably 5 to 15, most preferably 5 to 10, with the proviso that n and m are either the same integer or integers differing by 1 or 2,

(d) lowering the pH of the reaction mixture obtained in step (c) to a pH of 7 or less, preferably a pH of 2 to 4, and

(e) adding 1 to 2 Mol equivalents of a third alkylene oxide to obtain the quaternary fatty ammonium polyalkoxylate of formula I [$R_1R_2R_3N^+$-CHR_e-CHR_f-O-(CHR_e-CHR_f-O)$_p$H] X^- as defined above.

3. A method according to claims 1 or 2, wherein R_a, R_b, R_c, R_d, R_e, R_f are H.

4. A method according to any preceding claim, wherein the first and second and third alkylene oxide are independently of each other EO or PO, preferably EO and/or wherein the fatty amine is a (C6-24)alkyl- or (C6-24)alkenylamine preferably oleylamine.

5. A method according to any preceding claim, wherein the fatty amine in step (a) is dried in vacuo at a temperature of from 40 to 140°C, preferably 80 to 140°C, prior to subjecting it to step (b), and/or wherein step (b) is performed at a pressure of 2.5 bar or less.

6. A method according to any preceding claim, wherein the basic catalyst is selected from alkaline salts and alkali metal alkoxylates such as NaH, NaOH, NaOEt, NaOMe, KH, KOH, KOtBu, KOEt, CaO, CaH, $Ca(OH)_2$,$Ca(OCH(CH_3)_2)_2$, preferably NaOH an KOH.

7. A method according to any preceding claim, wherein in step (d) the pH is lowered by adding a mineral acid, preferably selected from hydrochloric acid, hydrobromic acid, nitric acid, phosphoric acid, sulfuric acid, boric acid, hydrofluoric acid, perchloric acid, or an organic acid, preferably selected from formic acid, acetic acid, 2-ethylhexanoic acid, lactic acid.

8. A method according to any preceding claim, wherein the temperature during addition of the first, second and third alkylene oxide, is less than 150°C, such as 100 to 150°C, preferably 120 to 150°C.

9. A quaternary fatty ammonium polyalkoxylate having 2 symmetrical alkoxylate chains obtained according to a method of claims 1 to 10.

10. Surfactant composition comprising one or more quaternary fatty ammonium polyalkoxylates having 2 symmetrical alkoxylate chains.

11. Surfactant composition according to claim 12, wherein the one or more quaternary fatty ammonium polyalkoxylates are of formula I $[R_1R_2R_3N^+\text{-}CHR_e\text{-}CHR_f\text{-}O\text{-}(CHR_e\text{-}CHR_f\text{-}O)_pH]\ X^-$, wherein

R_1 is a linear or branched, saturated or unsaturated, aliphatic or aromatic, substituted or unsubstituted C(6-24) hydrocarbon radical or a mixture thereof,

R_2 is a group of formula $-CHR_a\text{-}CHR_b\text{-}O\text{-}(CHR_a\text{-}CHR_b\text{-}O)_nH$ and R_3 is a group of formula $-CHR_c\text{-}CHR_d\text{-}O\text{-}(CHR_c\text{-}CHR_d\text{-}O)_mH$,

n and m are an integer of from 4 to 60, e.g. 4 to 40, preferably 4 to 20, more preferably 5 to 15, most preferably 5 to 10, with the proviso that n and m are either the same integer or integers differing by 1 or 2,

R_a, R_b, R_c, R_d, R_e, R_f are independently of each other H or Me,

p is 0 or 1, and

X^- is a counterion selected from the group consisting of species generated from a mineral acid or organic acid.

12. Surfactant composition according to claim 11, wherein R_a, R_b, R_c, R_d, R_e, R_f are H.

13. Surfactant composition according to claims 11 or 12, wherein the mineral acid is selected from hydrochloric acid, hydrobromic acid, nitric acid, phosphoric acid, sulfuric acid, boric acid, hydrofluoric acid, perchloric acid, and the organic acid is selected from formic acid, acetic acid, 2-ethylhexanoic acid, lactic acid.

14. Surfactant composition according to any one of claims 10 to 13 comprising at least one further component or additive, preferably selected from nonionic, cationic or anionic surfactants, deposit dispersant, pH adjusting agents and pH buffers including organic and inorganic salts; non-aqueous solvents, perfumes, perfume carriers, optical brighteners, coloring agents such as dyes and pigments, opacifying agents, hydrotropes, antifoaming agents, viscosity modifying agents such as thickeners, enzymes, anti-spotting agents, anti-oxidants, anti-corrosion agents.

15. Use of a quaternary fatty ammonium polyalkoxylate of formula $[R_1R_2R_3N^+\text{-}CHR_e\text{-}CHR_f\text{-}O\text{-}(CHR_e\text{-}CHR_f\text{-}O)_pH]\ X^-$ according to claim 9 or a surfactant composition according to any one of claims 10 to 14 as softeners, in personal care products, as deposit dispersant, as anti-corrosion agents in water cooling systems, or in agrochemical formulations.

Figure 1

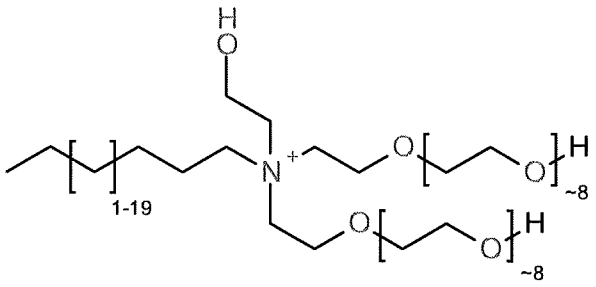
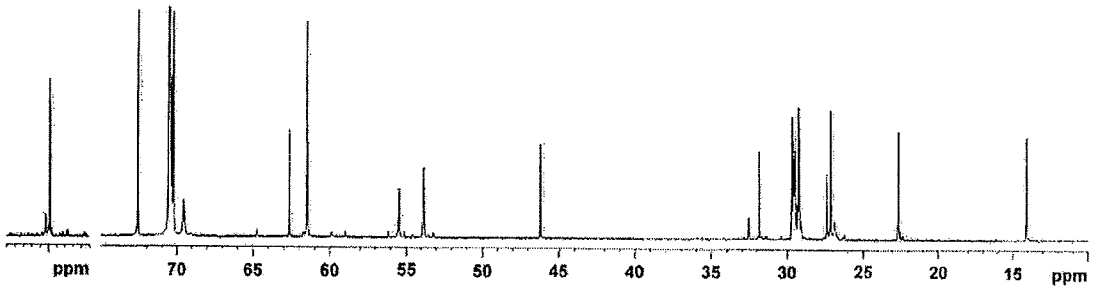
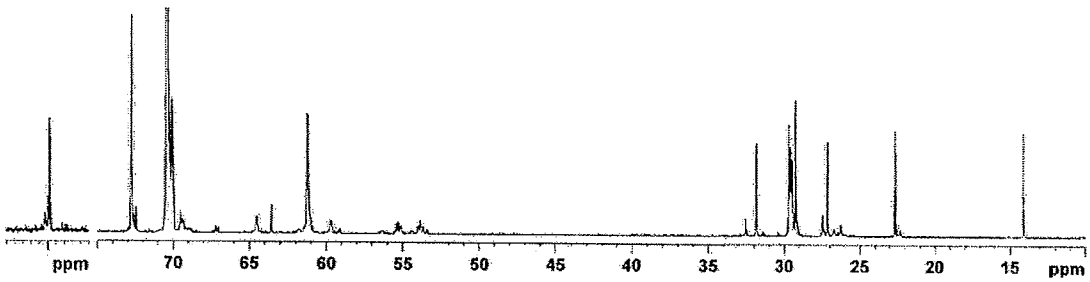


Figure 2

A


ppm
70
65
60
55
50
45
40
35
30
25
20
15
ppm

B


ppm
70
65
60
55
50
45
40
35
30
25
20
15
ppm

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/051762

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C209/12 C07C211/63
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07C

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 873 020 A (MUGGLI IMELDA A [US]) 10 October 1989 (1989-10-10) column 1, line 12; column 4 rection scheme;; claims 1-8; examples 1-8	1-11,15
X	WO 84/02701 A1 (AKZONA INC [US]) 19 July 1984 (1984-07-19) page 2, line 5 - page 3, line 13; page 4, lines 1-5;; claims 1-23; examples 1-26	9-13
A	DE 20 52 321 A1 (HENKEL & CIE. GMBH) 27 April 1972 (1972-04-27) cited in the application claims 1-3; examples 1-10	1-15

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
8 April 2015	17/04/2015

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

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PCT/EP2015/051762

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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