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(21) International Application Number: PCT/US98/02366 (22) International Filing Date: 11 February 1998 (11.02.98) (30) Priority Data: 9702731.2 11 February 1997 (11.02.97) GB (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): HEINZMAN, Stephen, Wayne [US/GB]; Deleval Old Vicarage, Seaton Sluice, Whitley Bay NE26 4QW (GB). INGRAM, Barry, Thomas [GB/GB]; 47 Western Way, Whitley Bay, Tyne & Wear NE26 1JE (GB). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: DETERGENT COMPOUND		
(57) Abstract <p>The present invention relates to cationic surfactants, containing at least one quaternary amine group and at least one primary, secondary or tertiary amine group. The surfactants may be used in any application where surfactancy is required. In particular they may be used in cleaning or detergent compositions or components thereof.</p>		

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Detergent Compound

Technical field

The present invention relates to a polyamine cationic surfactant, containing at least one quaternary amine group and at least one primary, secondary or tertiary amine group and methods for making them. The surfactants may be used in any application where surfactancy is required. In particular they may be used in cleaning or detergent compositions or components thereof.

Background to the invention

The satisfactory removal of greasy soils/stains, that is soils/stains having a high proportion of triglycerides or fatty acids, is a challenge faced by the formulator of detergent compositions for use in laundry and dish washing methods. Surfactant components have traditionally been employed in detergent products to facilitate the removal of such greasy soils/stains. In particular, surfactant systems comprising cationic surfactants have been described for use in greasy soil/stain removal.

A wide selection of surfactants for use in detergents can be found in the literature, but the reality is that many such surfactants are chemicals which are not always suitable in detergents, because of certain properties they have (such as instability in acidic or basic environment, incompatibility with bleach, malodour problems, biodegradability problems). Thus, the challenge to the detergent manufacturer seeking improved performance has been increased by these various factors. For example, some non-biodegradable ingredients have fallen into disfavour. As a result, the manufacturer is somewhat more limited than the literature would suggest in the selection of effective, yet affordable, ingredients.

A variety of cationic surfactants are suggested to be usable in detergents. One group of cationic surfactants which is widely studied is the group consisting of quaternary ammonium or imidazolinium compounds, which are often designed for speciality use. For example, various quaternary ammonium surfactants have been

suggested for use in shampoo compositions and are said to provide cosmetic benefits to hair.

US-A-4,228,042 discloses biodegradable cationic surfactants, including cationic ester surfactants for use in detergent compositions to provide greasy/oily soil removal. For example, US 3,567,729 discloses diquatery ammonium compounds for use in detergents. For example, US 5,068,431 describes quatery ammonium compounds, containing amphoteric amine oxide groups.

The Applicants have now found that certain polyamine cationic compounds, containing at least one cationically charged quatery amine group and at least one primary, secondary or tertiary amine group are very good surfactants, suitable for use in cleaning or detergent compositions. These compounds are found to be very surface active under alkaline washing conditions, and they are found to give excellent cleaning performance benefits. This is believed to be due to the compounds containing both a positively charged group and a neutral, more hydrophobic group.

Furthermore, several examples of these surfactants are found to be more biodegradable and to have a very low aquatic toxicity, relative to most quatery amine compounds.

It has been found that the stability of the polyamine cationic surfactants is not affected by changes of the pH. Furthermore, it has been found that, depending on their structure, most of the polyamine cationic compounds of the present invention and detergent compositions containing these polyamine cationic surfactants, are stable under standard storage and washing conditions.

Furthermore, it has been found that the polyamine cationic surfactants can be compatible with bleach, especially oxygen-based bleaches, and with certain bleach activators.

The polyamine cationic surfactants can be obtained via various efficient synthesis routes, and the production of these compounds can be very cost-effective.

All documents cited in the present description are, in relevant part, incorporated herein by reference.

Summary of the Invention

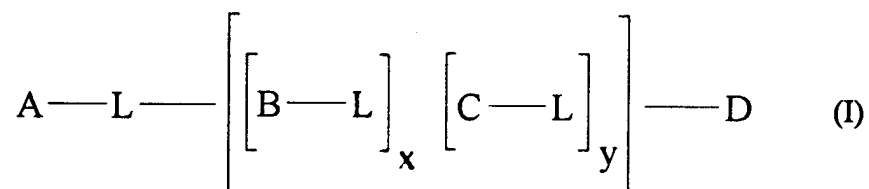
The present invention relates to polyamine cationic surfactants, containing at least one quaternary amine group and at least one primary, secondary or tertiary amine group. The invention also relates to methods of making the polyamine cationic surfactants. The polyamine cationic compounds of the invention can be used as a surfactant in any composition where surfactancy is required, for example in cleaning or detergent compositions or components thereof.

Detailed description of the invention

Cationic surfactant

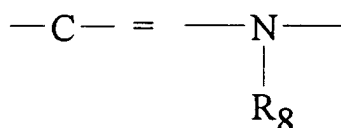
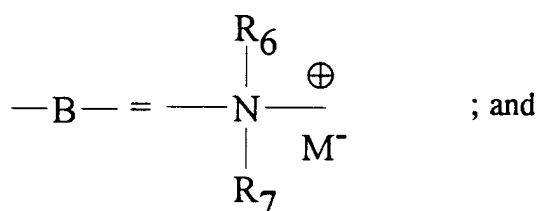
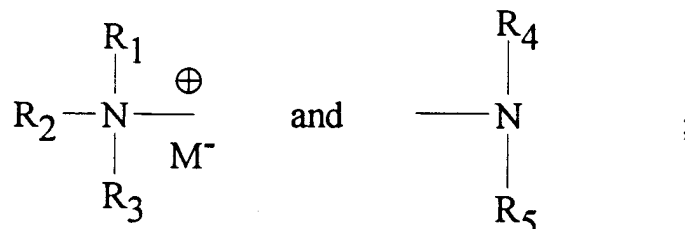
A cationic surfactant according to the present invention comprises at least one quaternized ammonium group and at least one primary, secondary or tertiary amine group, whereby not more than one linear or branched polyoxyalkylene group is present as substituent group.

Preferred cationic surfactant of the present invention are polyamine cationic surfactants of the general formula (I):



wherein L is a linking unit, and each L is independently selected from the group consisting of C₂-C₃₀ linear or branched alkylene, alkenylene, alkarylene, aralkylene, arylene, (poly) hydroxyalkylene, (poly) alkyleneoxy, (poly) hydroxy alkenylene; L can be substituted by one or more A, B, C or D units; x is a number

from 0 to 10, y is a number from 0 to 10; and wherein the units A- and D- are each independently selected from



wherein R₁, R₂, R₃, R₄, R₅, R₆, R₇ and R₈ are independently selected from the group consisting of C₁-C₃₀ linear or branched alkyl, alkenyl, alkaryl, aralkyl, aryl, (poly) hydroxyalkyl, (poly) hydroxy alkenyl, alkoxy group and hydrogen, one of R₁, R₂, R₃, R₄, R₅, R₆, R₇ or R₈ can be a linear or branched polyoxyalkylene group with from 2 to 26 oxyalkylene units or R₁ and R₂, R₁ and R₂ and R₃, R₄ and R₅ or R₆ and R₇ form together with the nitrogen atom part of a ring structure; or R₃ is not present and R₁ or R₂ is double bonded to the nitrogen; or R₇ is not present and R₆ is double bonded to the nitrogen; or R₅ is not present and R₄ is double bonded to the nitrogen; or, when x and y are 0, R₁ or R₂ or R₃ and R₄ or R₅ form together with the nitrogen atoms of A and D part of a ring structure; M⁻ is one or more counterions, and at least one A or D comprises a quaternized ammonium group in which none of R₁, R₂ or R₃ is hydrogen, or at least one B is present in which neither R₆ nor R₇ is hydrogen, and at least one A or D comprises a primary, secondary or tertiary amine group, or at least one C is present.

The units B-L and C-L are linked when both are present (i.e. when x and y do not equal 0), and they can be randomly present along the chain between the end units A-L and D.

Preferably, the value of x+y is from 1 to 4. Preferably, when x+y is greater than 1, at least one of present groups A, B, C or D is a secondary or primary ammonium group.

More preferably, x=0 and y is a number from 1 to 4. Even more preferably, both x and y are 0.

If x+y does not equal 0, it is preferred that the surfactant comprises only one quaternary group A or D.

Preferably R₆, R₇ and/or R₈ are each independently selected from a C₁-C₆, more preferably C₁-C₃ alkyl, alkoxyalkyl or (poly) hydroxyalkyl group or, most preferably hydrogen.

Preferably, R₁ is a C₆-C₁₄ alkyl, (poly) hydroxyalkyl or alkoxy group or an aralkyl group, most preferably a 2-ethylhexyl group, R₂ and R₃ are each independently C₁-C₆, more preferably C₁-C₃ alkyl or hydroxyalkyl groups and preferably R₄ and R₅ (and R₆, R₇ and R₈ when present) are each independently C₁-C₆, more preferably C₁-C₃ alkyl, alkoxyalkyl or (poly) hydroxyalkyl groups or, most preferably, hydrogen atoms.

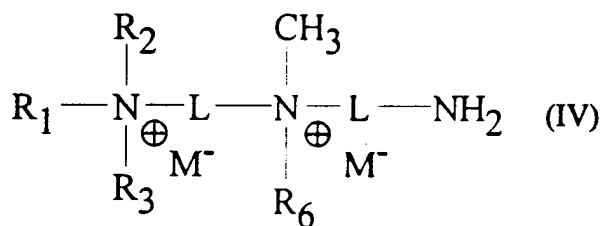
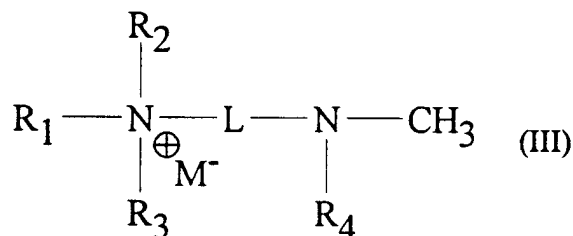
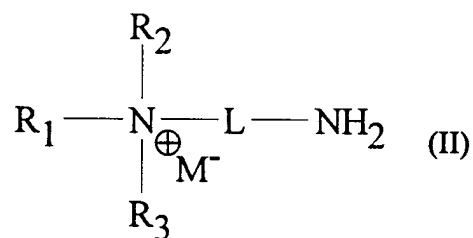
In a further preferred alternative, R₄ is preferably a C₆-C₁₄ alkyl, (poly) hydroxyalkyl, alkoxy group or an aralkyl group, most preferably a 2-ethylhexyl group R₅ is preferably a C₁-C₆, more preferably a C₁-C₃ alkyl, (poly) hydroxyalkyl group or hydrogen and R₁, R₂ and R₃ (and R₆, R₇ and R₈ when present) are each independently preferably C₁-C₆, more preferably C₁-C₃ alkyl, alkoxyalkyl or (poly) hydroxyalkyl groups or aralkyl groups.

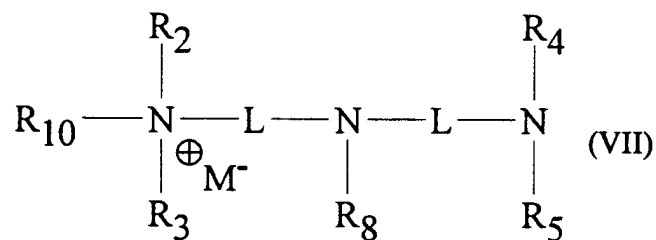
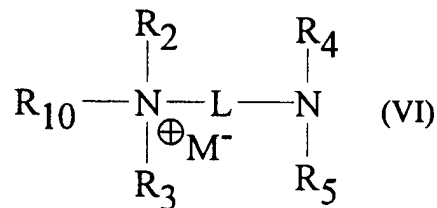
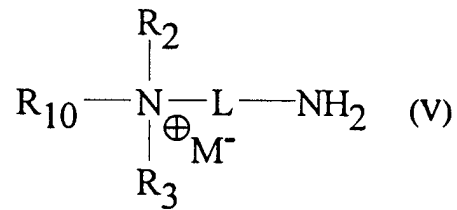
When R₁ and R₂, R₁ and R₂ and R₃, R₄ and R₅ or R₆ and R₇ form together with the nitrogen atom part of a ring structure, the ring structure is preferably a benzene ring structure, morpholino ring structure or a piperazino ring structure, or a substituted benzene or substituted morpholino or substituted piperazino ring structure.

When $x+y$ is 0 and R_1 or R_2 or R_3 and R_4 or R_5 form together with the nitrogen atoms of group A and D part of a ring structure, the ring structure is preferably a benzene ring structure, morpholino ring structure or a piperazino ring structure, or a substituted benzene or substituted morpholino or substituted piperazino ring structure.

L groups are independently preferably a C_2 - C_8 , more preferably a C_2 - C_4 linear or branched alkyl, hydroxy alkyl, alkoxy or hydroxy alkoxy group. If $x+y$ is 0, the l group is preferably a C_2 alkyl group. If group L comprises more than 2 carbon atoms, the surfactant preferably comprises at least one primary or secondary A, B, C or D group.

Examples of preferred polyamine cationic surfactants of the present invention are:



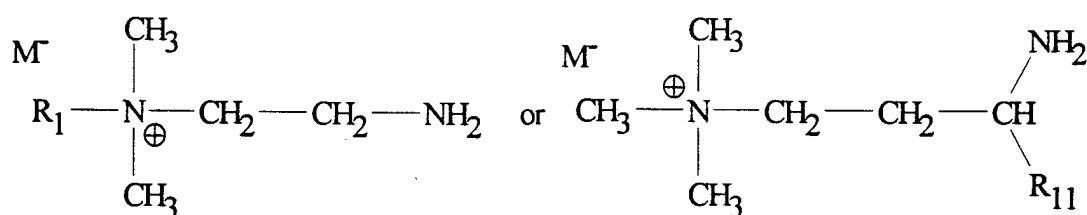


wherein R₁, R₄, R₆ and R₈ are as described above; R₂, R₃ and R₅ are independently selected from the group consisting of methyl, ethyl, hydroxyethyl, hydroxypropyl, polyhydroxy propyl, ethoxy, propoxy or 2,3,4,5,6-penta hydroxy hexyl, and are most preferably methyl or hydroxyethyl groups; R₁₀ is a methyl or hydroxyethyl group; L is as described above; R₁ and/or R₂ and/or R₄ are most preferably a 2-ethylhexyl group.

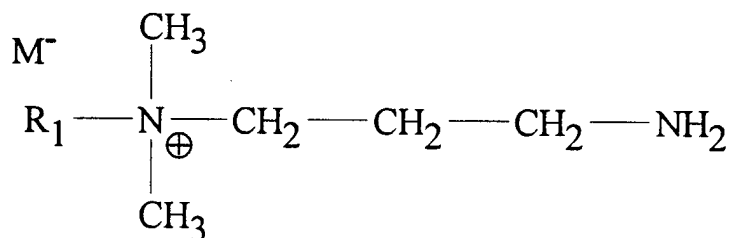
A highly preferred cationic polyamine surfactant is of formula VI, as defined above, wherein R₂ is a hydroxypropyl or hydroxyethyl group, R₃ and R₁₀ are methyl groups, L is C₂-C₃ alkyl group.

Highly preferred polyamine cationic surfactant are those of the formulas:

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or



wherein R_1 is as described above, preferably a C_2 - C_{14} , preferably C_6 - C_{14} linear or branched alkyl, (poly) hydroxy alkyl, alkoxy or aralkyl group; particularly preferred R_1 groups are hydroxyalkyl groups, where the alkyl groups have 2 to 5 carbon atoms, especially hydroxyethyl and hydroxypropyl are preferred; particularly preferred alkyl R_1 groups have up to 9 carbon atoms, most preferably R_1 is a 2-ethylhexyl group; and R_{11} is a C_2 - C_{14} alkyl, (poly) hydroxy alkyl, alkoxy or aralkyl group or a A or D unit as described above .

The anion M^- is a counterion for the cationically charged polyamine surfactant. Therefore, the number of M^- anions present will depend on the cationic charge of the polyamine surfactant, which depends on the groups A, B, C and D. The number of M^- anions will be at least 1. A preferred counterion is a halide anion, more preferably a sulphate anion.

Synthesis of the polyamine cationic surfactant

A variety of synthesis routes may be used for making the polyamine cationic surfactant of the present invention. Depending on which polyamine cationic surfactant reaction product is to be prepared and which starting material is available therefor, one synthesis route will be preferred over other possible routes and this choice will be well within the ambit of the skilled person given the examples below. The starting materials can be selected from a variety of (readily), commercially available compounds, depending on which polyamine cationic

surfactant needs to be prepared, and again, this selection is well within the ambit of the skilled person. Preferably, the starting material is an amine or diamine compound.

Preferred synthesis routes (A-D)

A. Reaction of two amine containing compounds

A preferred synthesis route is as follows. In a preferably organic solvent one or more primary or secondary amine compound and a quaternary halide or sulphate containing amine compound are mixed, preferably in a mole ratio of 1.5:1 to 3:1, to make them react together. When the reaction is complete, a basic compound is added, preferably sodium hydroxide, and the polyamine cationic surfactant reaction product can be removed from the reaction mixture by conventional methods.

Examples of this synthesis route are the reactions of any of hexylamine, octylamine, decylamine, dodecylamine or 2-ethylhexylamine with (3-bromo, chloro or sulphate propyl) trimethyl ammonium bromide, chloride or sulphate, in a ratio of about 2:1, in an organic solvent (ethanol), whereafter sodium hydroxide is added. Once the reaction is substantially completed (after reacting for up to 24 hours), the organic solvent and the possibly unreacted amine compound are removed from the reaction mixture via evaporation, and washed with (for example) diethyl ether, to yield a white solid diamine cationic surfactant, i.e. a (1-hexyl, octyl, decyl, dodecyl or 2-ethylhexyl amine) (3-trimethylamine) propane.

B. Alkylation of a diamine

Another preferred synthesis route is as follows.

A diamine compound and an alkylating agent are mixed in an organic solvent, preferably the diamine to alkylating agent are in a mole ratio of from 3.5:1 to 1.1:1. When the reaction is completed the polyamine cationic surfactant reaction product can be removed from the reaction mixture by conventional methods.

Examples of this synthesis are the reactions of any of 1-bromo or chloro hexane, octane, decane, dodecane or tetradecane or 2-ethylhexylbromide with tetramethylpropanediamine in an organic solvent (ethanol). The mole ratio of the

reactants is preferably about 1:1. Once the reaction is substantially completed, the organic solvent and any unreacted amine compound are removed from the reaction mixture via evaporation. The remaining product is then washed with (for example) diethyl ether, to yield the diamine cationic surfactant, i.e. hexyl, octyl, decyl dodecyl, tetradecyl 2-ethylhexyl, tetramethyl propanediamine.

C. Preparation of an imine, reduction and alkylation

A further preferred synthesis route is as follows.

In an organic solvent an aldehyde compound and a diamine compound are mixed in a mole ratio of from 2:1 to 1:2, whereby an imine is formed. The imine reaction product is reduced to a secondary diamine with a reducing agent. The secondary diamine product is then selectively alkylated on the secondary amine with an alkylating agent such as formaldehyde/ formic acid. The diamine is then quaternised/ alkylated using an alkylating agent to form a diamine cationic surfactant.

Examples of this synthesis route are the reactions of any of 2-ethylhexanal, hexanal, octanal, decanal or dodecanal with N,N, dimethylene diamine in an organic solvent (toluene), in a mole ratio of about 1:1. Once the reaction is substantially completed, the solvent is removed and borohydride is added to effect the reduction step. The reduced reaction product is then neutralised with formic acid and formaldehyde. Then, methyl bromide/ chloride is added to the reaction product to yield a white solid diamine cationic surfactant, i.e. N'-hexyl, octyl, decyl, dodecyl or ethylhexyl N,N, dimethylethylene diamine.

D. Selective alkylation of diamine

Yet another preferred synthesis route is as follows:

In an organic solvent a tertiary/primary alkyl diamine and an anhydride, acid, methyl ester or acid chloride are reacted, whereby the primary amine group is acylated to produce an amide compound. The reaction product is then selectively alkylated with an alkylating agent, and the amide product is hydrolysed using a mineral acid, to produce a diamine cationic surfactant.

An example of this synthesis route is the reaction of the N,N dimethylethylene diamine with acetic anhydride in an organic solvent (toluene), followed by

alkylation in an organic solvent (ethanol) with bromo- or chloro- hexane, octane, decane or dodecane to yield a quaternary amine amide. This reaction product is hydrolysed using hydrobromic acid in water, to produce a diamine cationic surfactant, i.e. a N,N,N, hexyl, octyl, decyl or dodecyl-dimethyl ethylene diamine.

Examples of small scale synthesis of preferred polyamine cationic surfactants

Example 1

1.1

Into a 250ml round bottom flask fitted with reflux condenser and drying tube was placed 1-bromohexane (10.0g, 0.061 mol) and tetramethylpropanediamine (8.68g, 0.067 mol) in 100ml ethanol. The mixture was refluxed for 72 hours. Ethanol was removed by rotary evaporation, adding additional ethanol to remove unreacted amine. The resultant sticky solid was triturated with diethyl ether, but remained a syrup. Analysis by 270 M Hz¹ H NMR in CDCl₃ gave the following peaks: δ 0.9 (t, 4H), 1.3-1.5 (bs), 1.7 (m, 2H), 1.95 (m, 2H), 2.25 (s, 6H), 2.4 (t, 2H), 3.4-3.7 (2s, m, 14H inc. ethanol).

This synthesis was also carried out using the following materials:

1.2 replacing bromohexane with other alkyl bromides:

Bromooctane	Yield 24%
Bromodecane	Yield 14%

1.3 replacing tetramethylpropanediamine with tetramethylethanediamine and using the following alkyl bromides:

<u>Alkyl Bromide</u>	<u>Yield</u>
Bromohexane	85%
Bromooctane	91%
Bromodecane	85%
Bromotetradecane	75%
2-Ethylhexylbromide	88%

Example 2

2.1

Into a 250 ml round bottom flask fitted with reflux condenser and drying tube was placed octylamine (7.50g, 0.58 mol) and (3-bromopropyl)trimethylammoniumbromide (10.15g, 0.0387 mol) in 100 ml ethanol. The mixture was refluxed for 1 day. Further octylamine (2.50g, 0.0193 mol) was added and the mixture refluxed for 1 day. Sodium hydroxide (1.56g) was added and the mixture filtered to remove the resultant precipitate. Ethanol was removed by rotary evaporation, adding additional ethanol to remove unreacted amine. The resultant sticky solid was triturated with diethyl ether, to yield a white solid, (10g, 87.60% yield). Analysis by 270 M Hz¹ H NMR in CD₃OD gave the following peaks: δ 0.9(t), 1.2-1.4(bs), 1.6(m), 2.0(m), 2.5-2.7(2m), 3.2(2s), 3.4(m).

This synthesis was also carried out with the following materials:

2.2 replacing octylamine with the following alkylamines.

Butylamine

Hexylamine

Decylamine

Dodecylamine

2-Ethylhexylamine

Detergent compositions and components thereof

The polyamine cationic surfactant of the present invention may be used in any application where surfactancy is required. For example, the polyamine cationic surfactant of the present invention can be used in detergent compositions or components thereof.

Depending on the type of detergent composition or component the polyamine cationic surfactant of the present invention can be present at a level of from 0.05% to 95% by weight of the composition or component.

The detergent compositions or components thereof can contain any of the traditionally known and used detergent ingredients or components. The precise nature of these components, and levels of incorporation thereof will depend on the physical form of the composition, and the precise nature of the washing operation for which it is to be used.

The detergent compositions or components thereof preferably contain one or more detergent components selected from additional surfactants, bleaches, bleach catalysts, bleach precursors, water-soluble and insoluble builders, chelants, organic polymeric compounds, enzymes, suds suppressors, lime soap dispersants, soil suspension and anti-redeposition agents, perfumes, brighteners and corrosion inhibitors.

The additional surfactant can be selected from anionic, nonionic, additional cationic, ampholytic, amphoteric and zwitterionic surfactants and mixtures thereof.

Where present, ampholytic, amphoteric and zwitterionic surfactants are generally used in combination with one or more anionic and/or nonionic surfactants.

pH of the detergent compositions

The detergent compositions preferably have a pH measured as a 1% solution in distilled water of at least 8.5, preferably from 9.0 to 12.5, most preferably from 9.5 to 11.0.

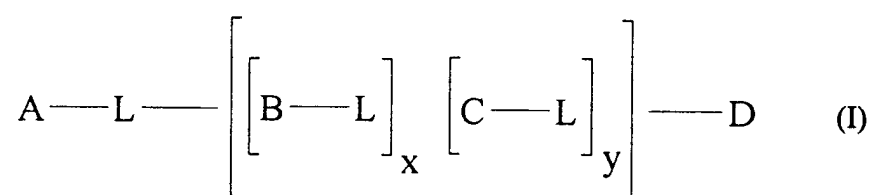
Form of the compositions

The detergent or cleaning compositions, comprising the polyamine cationic surfactant of the present invention, can take a variety of physical forms including granular, tablet, bar and liquid forms. The compositions are particularly the so-called concentrated granular detergent compositions adapted to be added to a washing machine by means of a dispensing device placed in the machine drum with the soiled fabric load.

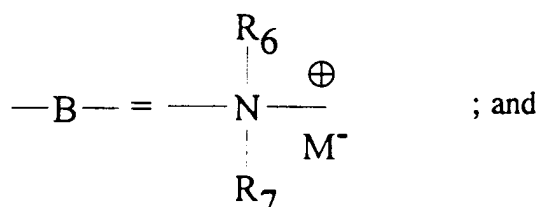
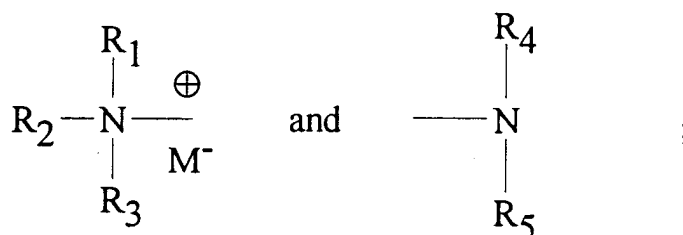
In general, granular detergent compositions in accordance with the present invention can be made via a variety of methods including dry mixing, spray drying, agglomeration and granulation.

What is claimed is:

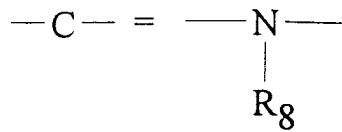
1. A cationic surfactant comprising at least one quaternized ammonium group and at least one primary, secondary or tertiary amine group, wherein not more than one linear or branched polyoxyalkylene group is present as substituent group.
2. A cationic surfactant according to Claim 1 of the general formula:



wherein L is a linking unit, and each L is independently selected from the group consisting of C₂-C₃₀ linear or branched alkylene, alkenylene, alkarylene, aralkylene, arylene, (poly) hydroxyalkylene, (poly) alkyleneoxy, (poly) hydroxy alkenylene; L can be substituted by one or more A, B, C or D units; x is a number from 0 to 10, y is a number from 0 to 10; and wherein the units A- and D- are each independently selected from:



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wherein R₁, R₂, R₃, R₄, R₅, R₆, R₇ and R₈ are independently selected from the group consisting of C₁-C₃₀ linear or branched alkyl, alkenyl, alkaryl, aralkyl, aryl, (poly) hydroxyalkyl, (poly) hydroxy alkenyl, alkoxy group and hydrogen, one of R₁, R₂, R₃, R₄, R₅, R₆, R₇ or R₈ can be a linear or branched polyoxyalkylene group with from 2 to 26 oxyalkylene units or R₁ and R₂, R₁ and R₂ and R₃, R₄ and R₅ or R₆ and R₇ form together with the nitrogen atom part of a ring structure; or R₃ is not present and R₁ or R₂ is double bonded to the nitrogen; or R₇ is not present and R₆ is double bonded to the nitrogen; or R₅ is not present and R₄ is double bonded to the nitrogen; M⁻ is one or more counterions, and at least one A or D comprises a quaternized ammonium group in which none of R₁, R₂ or R₃ is hydrogen, or at least one B is present in which neither R₆ or R₇ is hydrogen, and at least one A or D comprises a primary, secondary or tertiary amine group, or at least one C is present

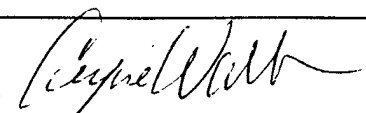
3. A polyamine cationic surfactant according to Claim 2 wherein x=0.
4. A polyamine cationic surfactant according to Claim 2 wherein x=0 and y=0.
5. A polyamine cationic surfactant according to any of Claims 2 to 4 wherein R₁ is a C₆-C₁₄ alkyl group.
6. A polyamine cationic surfactant according to any of Claims 2 to 5 wherein R₁ or R₄ is a 2-ethylhexyl group.
7. A polyamine cationic surfactant according to Claim 5 wherein R₄ and R₅ are, independently from each other, C₁-C₆ alkyl or (poly) hydroxyalkyl group or hydrogen atom.
8. A polyamine cationic surfactant according to any of Claims 5 or 7 wherein R₄ and R₅ are hydrogen.

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14. A process for preparing a polyamine cationic surfactant according to any of Claims 4 to 10 comprising the steps of
 - (1) reaction of a diamine with an anhydride to form an acylated diamine;
 - (2) selective alkylation of the acylated diamine to form an acylated and alkylated diamine; and
 - (3) hydrolysis of the acylated alkylated diamine to form a polyamine cationic surfactant according to any of Claims 4 to 10.
15. A detergent composition or component thereof, comprising the polyamine cationic surfactant according to any of Claims 1 to 10 and comprising one of more other detergent components.
16. A detergent composition according to Claim 15 in which the detergent composition is selected from the group of anionic, nonionic surfactants, water soluble and non-soluble builders and bleaching agents.
17. A method for preparing a detergent composition according to Claim 15 or Claim 16 comprising mixing the polyamine cationic surfactant according to any of Claims 1 to 10 with one or more other detergent components.
18. Detergent compositions produced according to Claim 17.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/02366

A. CLASSIFICATION OF SUBJECT MATTER IPC(6) : C11D 1/40, 1/42, 1/44, 1/48, 1/62 US CL : 510/504, 506 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) U.S. : 510/504, 506 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) STN structure search		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US H1313 A (JOHNSON ET AL) 03 May 1994 (03-05-94), column 3, line 22-column 5, line 33; column 7, line 22-column 8, line 10; column 14, line 36-column 15, line 22.	1-5
X	US 4,248,827 A (KITKO) 03 February 1981 (03-02-81), column 3, line 34-column 5, line 15; column 10, line 52-column 11, line 35.	1-5
A	US 4,960,526 A (PUENTES-BRAVO ET AL) 02 October 1990 (02-10-90), entire document.	
A	JP 06-123,071 A (KAO CORP) 06 MAY 1994 (06-05-94), entire document.	
A	JP 01-113,500 A (DAINICHISEIKA LTD) 02 May 1989 (02-05-89), entire document.	
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
A	document defining the general state of the art which is not considered to be of particular relevance	*T*
E	earlier document published on or after the international filing date	*X*
L	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Y*
O	document referring to an oral disclosure, use, exhibition or other means	*Z*
P	document published prior to the international filing date but later than the priority date claimed	*A*
		later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
		document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
		document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
		document member of the same patent family
Date of the actual completion of the international search		Date of mailing of the international search report
24 MARCH 1998		01 MAY 1998
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230		Authorized officer JOHN R. HARDEE  Telephone No. (703) 308-0661

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/02366**Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. Claims Nos.: 6-8 and 14-18
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- The additional search fees were accompanied by the applicant's protest.
 No protest accompanied the payment of additional search fees.