

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **89301533.9**

(51) Int. Cl.⁴: **C11D 1/835 , C11D 1/62 ,
C11D 1/66**

(22) Date of filing: **16.02.89**

(30) Priority: **23.02.88 GB 8804143**

(43) Date of publication of application:
27.09.89 Bulletin 89/39

(84) Designated Contracting States:
BE DE ES FR GB IT NL SE

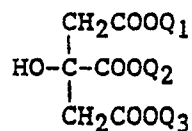
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(54) **Fabric conditioners.**

(57) This invention relates to an aqueous based fabric softening formulation comprising a water dispersible cationic softener, a non-ionic softener and optionally an electrolyte, the non-ionic softener being an alkoxyated dialkylcitrate of the formula:-



wherein Q₁, Q₂ and Q₃ are such that at least two of them are C₁₆-C₂₀ alkyl groups and the third is an alkoxy group of the formula (CH₂ CHR₁O)_nH wherein R₁ is H or CH₃ and n has a value from 1 to 15. These formulations can be used with conventional smectite type clay softeners.

EP 0 334 482 A1

FABRIC CONDITIONERS

This invention relates to compositions suitable for use in fabric conditioning.

Fabric softener formulations are usually aqueous based, contain a water dispersible cationic softener, a non-ionic softener and an electrolyte which enables the viscosity of the formulation to be controlled.

It has now been found that good fabric softening formulations may be formed by using a specific non-ionic softener without adversely affecting the fabric being softened or the softening process.

Accordingly, the present invention is an aqueous based fabric softening formulation comprising a water dispersible cationic softener, a non-ionic softener and optionally an electrolyte, characterised in that the non-ionic softener comprises an alkoxyated dialkylcitrate of the formula:-



wherein Q_1 , Q_2 and Q_3 are such that at least two of them are C_{15} - C_{20} alkyl groups and the third is an alkoxy group of the formula $(\text{CH}_2 \text{CHR}_1\text{O})_n\text{H}$ wherein R_1 is H or CH_3 and n has a value from 1 to 15.

In the non-ionic alkoxyated dialkyl citrates of the present invention, the alkoxy groups are preferably ethoxyl groups. The value of the alkoxy groups, n is preferably from 3 to 10, most preferably 5. Each alkyl group is preferably a dioctadecyl group.

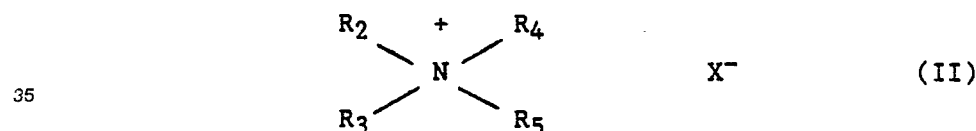
The amount of the dialkyl citrate supplement in the formulation is suitably from 5-60% w/w, preferably from 10-40% w/w based on the total surfactant content of the formulation.

The fabric conditioning formulation may contain in addition other surfactants such as an alkyl fatty acid alkoxyate, an alkylalkoxyate or mixtures thereof. Specific examples of such other surfactants include alkyl fatty acid ethoxylates and alkyl ethoxylates respectively.

The non-ionic alkoxyated dialkyl citrate is suitably used in conjunction with conventional water-dispersible cationic softeners such as the quaternary ammonium halides or the imidazolinium halides.

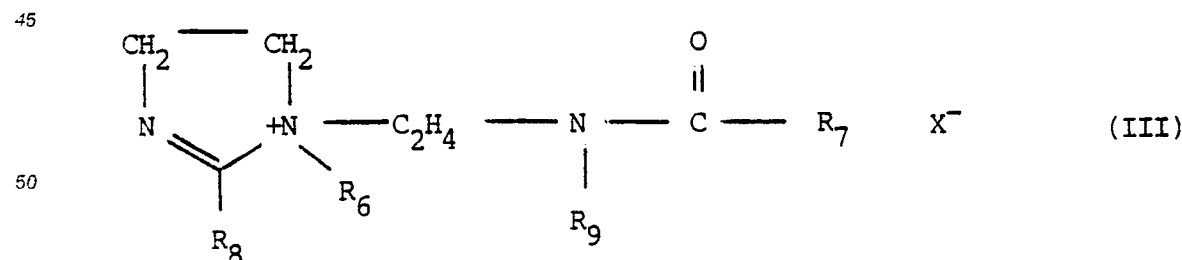
Thus, according to a further embodiment the present invention is an aqueous based fabric conditioning formulation comprising:

- (a) a water-dispersible cationic softener selected from
 (i) dihydrocarbyldialkylammonium salt of the formula:-



wherein R_2 and R_3 are the same or different C_{12} to C_{24} alkyl or alkenyl groups, which may optionally carry additional functional groups selected from -OH, -O-, -CONH and -COO-either as substituents or as part of the main alkyl or alkenyl chain, R_4 and R_5 are the same or different C_1 - C_4 alkyl groups, and X^- is an anion selected from a halide, methosulphate and ethosulphate and

- (ii) an alkylimidazolinium salt of the formula (III):

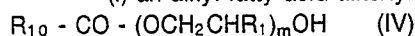


wherein R_6 is a C_1 - C_4 alkyl or hydroxyalkyl group, R_7 and R_8 are the same or different alkyl or alkenyl

groups containing from 8 to 25 carbon atoms, and R_3 is hydrogen or a C_1 - C_4 alkyl group and X^- is an anion, selected from a halide, methosulphate or ethosulphate;

- (b) an alkoxylated dialkyl citrate of the formula (I) above, and
 5 (c) one or more alkoxylates selected from:

(i) an alkyl fatty acid alkoxylate of the formula:

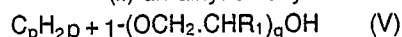


wherein R_{10} is a C_{11} - C_{19} alkyl or alkenyl group,

R_1 is H or $-CH_3$, and

10 m has a value from 1 to 6; and

(ii) an alkyl alkoxylate of the formula:



wherein R_1 is H or $-CH_3$

p is an integer from 16-20, and

15 q has a value from 1 to 15; and optionally,

(d) an electrolyte.

Examples of these cationic softeners of formula (II) above include ditallow dimethyl ammonium chloride;
 20 ditallow dimethyl ammonium methyl sulphate; dihexadecyl dimethyl ammonium chloride; dioctadecyl dimethyl ammonium chloride; dieicosyl dimethyl ammonium chloride; didocosyl dimethyl ammonium chloride; di(hydrogenated tallow) dimethyl ammonium methylsulphate; dihexadecyl diethyl ammonium chloride; di(coconut alkyl) dimethyl ammonium chloride. Ditallow dimethyl ammonium chloride, di(hydrogenated tallow alkyl) dimethyl ammonium chloride, di(coconut alkyl) dimethyl ammonium chloride and
 25 di(coconut alkyl) dimethyl ammonium methosulphate are preferred.

In a formulation containing the components (a), (b) and (c) above if the component (a) is represented by formula (II) each of R_2 and R_3 suitably represent a substituent in which more than 50%, preferably more than 75% of the groups are C_{16} or C_{18} alkyl or alkenyl groups. More preferably, each of the substituent groups R_2 and R_3 represent a mixture of alkyl and alkenyl groups, namely from 50-90% C_{18} alkyl or alkenyl
 30 groups and from 10 to 50% C_{16} alkyl or alkenyl groups.

Thus, the substituents R_2 and R_3 are most preferably represented by ditallow groupings, and substituents R_4 and R_5 are preferably methyl groups and the anion is preferably a chloride.

Thus, the preferred component (a) of formula (II) is ditallowdimethyl ammonium chloride.

Examples of the imidazolinium salts of formula (III) above include 1-methyl-1-(tallowylamido-) ethyl -2-
 35 tallowyl-4,5-dihydro imidazolinium methosulphate and 1-methyl-1-(palmitoylamido)ethyl -2-octadecyl-4,5-dihydro-imidazolinium chloride. Other useful imidazolinium materials are 2-heptadecyl-1-methyl-1-(2-stearyl-1-hydroxyethyl-1-oleyl-imidazolinium chloride. Such imidazolinium fabric softening components are described more fully in US Patent No. 4 127 489 and can be used in the formulations of the present invention.

40 The cationic quaternary salt components falling within (a) above are commercially available materials under the following trade names or Registered Trade marks: Arquad 2HT (ex AKZO); Noranium M2SH (ex CECA); Aliquat-2HT and the imidazolinium compounds falling within (a) are Varisoft 475 and Rewoquat W7500.

The formulations of the present invention may optionally include specific electrolytes to assist in
 45 controlling the viscosity of the product. The amount of electrolyte in the formulation is suitably from 0.01% to 0.5%, most preferably from about 0.02% to about 0.2%, measured as the anhydrous salt. Examples of electrolytes that may be used include lithium chloride, calcium chloride, magnesium chloride, aluminium chloride and mixtures thereof.

In the alkyl fatty acid alkoxylates of formula (IV) it is preferable to use the ethoxylates, i.e. compounds
 50 in which R_1 is H. The value of alkoxy groups, m, in the alkyl fatty acid alkoxylates is preferably from 1-3. The fatty acid used is preferably a tallow fatty acid, which is a mixture of 25% palmitic acid, 39% oleic acid, 19% stearic acid, 4.5% linoleic acid and 3% myristic acid. Such a fatty acid is sold commercially as T20 by Procter and Gamble.

As for the alkyl alkoxylates of formula (V), it is preferable to use an alkyl ethoxylate, i.e. R_1 in formula
 55 (V) is H. The value of the alkoxy group, q, is preferably from 1 to 4.

When using a fabric conditioning formulation in which all the three components (a), (b) and (c) are normally present, the following weight percentages of each based on the total weight of (a), (b) and (c) are suitably used:-

(a) 10 to 90%

(b) 5 to 60%

(c) 5 to 60%

Preferably (a), (b) and (c) are present in the following weight percentages of the total weight of (a), (b) and (c)..

(a) 25 to 80%

(b) 10 to 40%

(c) 10 to 40%

More preferably, (a), (b) and (c) are present in the following weight percentages based on the total weight of (a), (b) and (c)

(a) 40 to 70%

(b) 10 to 30%

(c) 10 to 30%

Compositions according to the present invention may be prepared by blending, e.g. by melting (a), (b) and (c) at a temperature in the range 50 to 60° C.

The compositions according to the present invention may be dispersed in water by mixing the components (a), (b) and (c) in water with moderate shearing at elevated temperature, for example, in the range 40 to 50° C.

The total amount of (a), (b) and (c) in the water is preferably from 2 to 10% by weight.

Thus as another aspect of the present invention, a fabric conditioner comprises a total of 2 to 10% by weight of (a), (b) and (c) in an aqueous dispersion.

The fabric conditioners of the present invention may be used in conjunction with clays to improve the softness of the fabrics conditioned. As clays may be used any aluminosilicate type material which has the ability to impart softening to fabrics laundered with a formulation containing the same. Clays having an ion-exchange capacity of at least 50 meq/100g of clay (milliequivalents per 100g of clay) are preferred. Specific examples of such clays include smectite type clays. These latter clays are multi-layered clays which layered structure is capable of increasing the volume thereof several-fold by their ability to swell or expand when in contact with water and thereby form a thixotropic gelatinous substance.

Such clays are well known in the art and are described for example in GB-A-12201172, GB-A-1400898, GB-A-1462484, GB-A-2132629 and EP-A-225142 which are incorporated herein by reference. Specific examples of clays that may be used in the present invention include bentonite, montmorillonite, nontronite, volchonskoite, saponite, hectorite, sanconite and vermiculite, and mixtures thereof. The amount of clay present in the formulation is suitably from 1-50% w/w, preferably from 2-30% w/w of the total formulation.

The clay-based formulations of the present invention may be used as part of a single liquid detergent system which incorporates the function of cleansing the fabrics washed as well as softening. Other components in such a formulation include one or more surfactants and a builder salt. In this case, the water-dispersible cationic softner may optionally be omitted.

Other components present in the fabric conditioner formulation may include a dye and a perfume.

Examples

1. Preparation

1.1 Ditalow dimethylammonium chloride

Ditalow dimethylammonium chloride (each of R₂ and R₃ = more than 75% C₁₃ or C₁₅ alkyl or alkenyl group) can be prepared in various ways well known in the art and is a commercially available material, for example, Ciba Geigy Arquad 2HT (Regd TM).

1.2 Tallow fatty acid ethoxylate

Tallow fatty acid (25% palmitic acid, 39% oleic acid, 19% stearic acid, 4.5% linoleic acid, 3% myristic acid), e.g. Procter and Gamble T20 acid, was treated with potassium hydroxide (0.3%) at 100° C, under

vacuum to remove water. Ethoxylation was performed using standard procedures with a boron trifluoride catalyst at 170 to 180 °C under 35 to 40 p.s.i.g pressure in an autoclave, 3 moles of ethylene oxide being added per mole of fatty acid.

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1.3 Synthesis of octadecylethoxylate

Octadecanol was treated with potassium hydroxide (0.3%) at 100 °C, under vacuum to remove water. Reaction, in an autoclave, was performed with 3 moles of ethylene oxide being added per mole of alcohol
10 at 160 to 170 °C and 35 to 40 p.s.i.g pressure.

1.4 Synthesis of ethoxylated dioctadecyl citrate

15 Dioctadecyl citrate was prepared by heating 2 moles of octadecanol with 1 mole of citric acid at 155 °C for 1.5h, so that the calculated quantity of water distills, according to the method of Borchert and Hartford, World Surfactants Congress, Munich, 6 - 8th May, 1984, Volume II, p 147. The product was a mixture of diesters (57%), monoesters (34%) and triesters (9%) of citrate.

The ethoxylated dioctadecyl citrate, was prepared by reaction of dioctadecyl citrate in an autoclave with
20 5 moles of ethylene oxide at a temperature of 170 - 180 °C and a pressure of 35 - 40 psig according to standard procedures. (See for example, Malkemus, J.Amer. Oil Chemists' Soc., 1956, 33, 571). Potassium hydroxide (0.2%) was used as the catalyst.

25 2. Softening Tests

SOFTENING TEST 2.1

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Test Solution

Ditallowdimethylammonium chloride (available as a 75% mixture of the ammonium halide and 25% propan-2-ol) was heated at 50 °C and mixed under low shear conditions with the tallow fatty acid ethoxylate
35 and the octadecyl ethoxylate.

A 5% (by total weight) dispersion was formed in water heated to 40 °C, with moderate shearing and contained 3% by weight of ditallow dimethylammonium chloride, 1% by weight of tallow fatty acid ethoxylate (with m = 1 in formula (IV)), and 1% by weight of octadecylethoxylate (with q = 3 in formula (V)).

40 When cool, 4g of this 5% dispersion was further diluted with 996g of water to obtain a test solution which simulates a typical concentration of fabric conditioner existing in a washing machine rinse cycle.

Comparative Solution

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A comparative solution was prepared by diluting 4g of 5% by weight in water dispersion of the ditallowdimethylammonium chloride in 996g of water.

The test solution and the comparative solution were used to soften test cloths.

16 Sixteen terry towel cloths were washed twice in a commercial heavy duty detergent powder (not
50 containing softener) to remove any coating applied during manufacture. Eight of the cloths were soaked in the test solution and eight of the cloths were soaked in the comparative solution at a cloth/liquor ratio of 150g/1.5 litres for 10 minutes with gentle agitation using a glass rod. They were subsequently removed, tumble dried and divided into eight in order that each of the softening panellists used the same sample.

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Pair Comparison Tests

The softening test procedure entitled pair comparison tests was carried out using panels of 8 persons. Panel members were required to compare the softness of two cloths A and B (one being a test cloth, the other a comparison cloth) and rank them as follows:-

5	A is definitely softer than B	Score +2
	A is possibly softer than B	Score +1
	No difference	Score 0
	A is possibly harsher than B	Score -1
10	A is definitely harsher than B	Score -2

Scores for each cloth were totalled, averaged and the 95% confidence limit calculated.

On a scale of -2 to +2 the test solution scored +0.35 in a panel test compared with +0.05 for the comparative solution.

15 The viscosity of this new formulation at a shear rate of 1 sec^{-1} was 2100 milliPascal sec, compared with 550 milliPascal sec for the comparative solution.

20 SOFTENING TEST 2.2

Test Solution

25 A test solution was prepared using the method described in 2.1 above to form a dispersion in water containing 5% by weight of the total of the ditallowdimethylammonium chloride, the tallow fatty acid ethoxylate, and the ethoxylated dioctadecylcitrate. The dispersion contained 2% by weight of ditallowdimethylammonium chloride, 2% by weight of tallow fatty acid where ($m = 3$ in formula (IV)) ethoxylate and 1% by weight of ethoxylated dioctadecylcitrate (where $n = 5$ in formula (I)). 4g of this 5% dispersion was diluted in 996g of water.

Comparative Solution

A comparative solution was prepared as in Softening Test 2.1 above.

35 The test solution and the comparative solution were used to soften test cloths. Pair comparison tests were carried out using panels of 8 persons as in Softening Test 2.1 above.

On scale of -2 to +2 the test solution scored +0.18 in a panel test compared with +0.05 for the comparative solution.

40 The viscosity of this new formulation at a shear rate of 1 sec^{-1} was 2500 milliPascal sec compared with 550 milliPascal sec for the comparative solution.

The test solution showed a significant viscosity enhancement and a significantly improved softening performance over the comparative solution.

45 SOFTENING TEST 2.3

Softening Test 2.2 was repeated, but using a dispersion in water containing 3% by weight of the ditallowdimethylammonium chloride, 1% by weight of tallow fatty acid ethoxylate (where $m = 3$ in formula (IV)), and 1% by weight of ethoxylated dioctadecylcitrate (where $n = 5$ in formula (I)). This composition was 50 not significantly different in performance from the comparative solution in a panel test, although less ditallowdimethylammonium chloride was used.

The viscosity of this new formulation at 1 sec^{-1} was 2000 milliPascal sec compared with 550 milliPascal sec for the comparative solution, showing significant viscosity enhancement.

55 SOFTENING TEST 2.4

Softening Test 2.2 was repeated, but using a dispersion in water containing 4% by weight of the

ditallowdimethylammonium chloride without any fatty acid ethoxylate and 1% by weight of ethoxylated dioctadecylcitrate (where $n = 5$ in formula (I)).

The viscosity of this new formulation at 1 sec^{-1} was 176 milliPascal sec compared with 550 milliPascal sec for the comparative solution.

5 The test solution and the comparative solution were used to soften test cloths. Pair comparison tests were carried out using panels of 8 persons as in Softening Test 2.1 above.

On a scale of -2 to +2 the test solution scored *0.95 in a panel test compared with +0.35 for the comparative solution.

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SOFTENING TEST 2.5

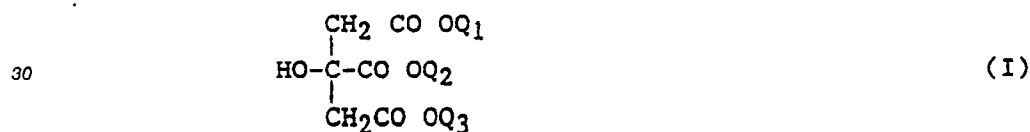
Softening Test 2.2 was repeated, but using a dispersion in water containing 4% by weight of the ditallowdimethylammonium chloride without any fatty acid ethoxylate and 1% by weight of ethoxylated
15 dioctadecylcitrate (where $n = 10$ in formula (I)). This composition was not significantly different in performance from the comparative solution in a panel test, although less ditallowdimethylammonium chloride was used.

The viscosity of this new formulation at 1 sec^{-1} was 504 milliPascal sec compared with 550 milliPascal sec for the comparative solution.

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Claims

1. An aqueous based fabric softening formulation comprising a water dispersible cationic softener, a
25 non-ionic softener and optionally an electrolyte characterised in that the non-ionic softner comprises an alkoxylated dialkylcitrate of the formula:



wherein Q_1 , Q_2 and Q_3 are such that at least two of them are C_{15} - C_{20} alkyl groups and the third is an
35 alkoxyl group of the formula $(\text{CH}_2 \text{ CHR}_1 \text{O})_n \text{H}$ wherein R_1 is H or CH_3 and n has a value from 1 to 15.

2. A fabric softening formulation according to claim 1 wherein the Q_1 and Q_3 represent C_{15} - C_{20} alkyl groups and Q_2 represents the alkoxyl group.

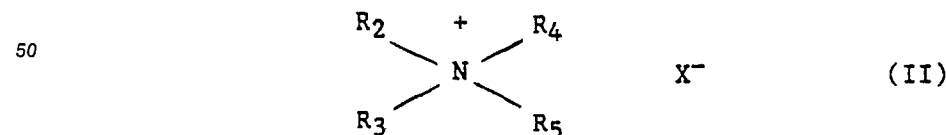
3. A fabric softening formulation according to claim 1 or 2 wherein the alkoxyl group is an ethoxyl group.

40 4. A fabric softening formulation according to any one of the preceding claims wherein each of the alkyl groups in formula (I) is derived from octadecyl alcohol.

5. A fabric softening formulation according to any one of the preceding claims wherein the alkoxydialkylcitrate is present in an amount from 5-60% w/w based on the total surfactant content of the formulation.

6. An aqueous based fabric softening formulation according to any one of the preceding claims, said
45 formulation comprising

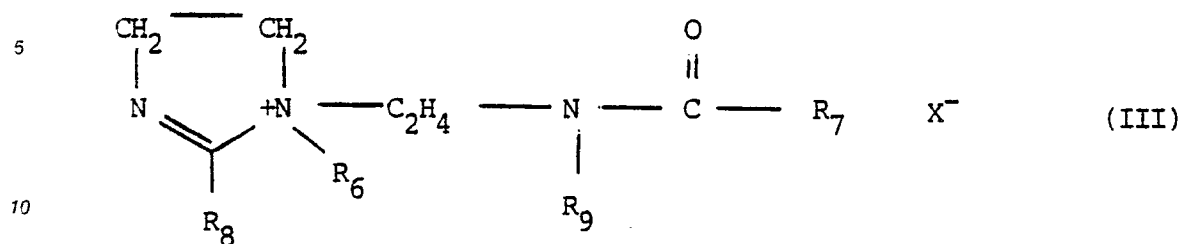
(a) a water dispersible cationic softner selected from
(i) dihydrocarbyldialkylammonium salt of the formula:



55 wherein R_2 and R_3 are the same or different C_{12} to C_{24} alkyl or alkenyl groups, which may optionally carry additional functional groups selected from -OH, -O-, -CON- and -COO- either as substituents or as part of the main alkyl or alkenyl chain,

R_4 and R_5 are the same or different C_1 - C_4 alkyl, hydroxyalkyl and polyoxyalkylene groups, and X^- is an

anion selected from a halide, methosulphate and ethosulphate and (ii) an alkylimidazolium salt of the formula (III):



wherein R_6 is a C_1 - C_4 alkyl or hydroxyalkyl group, R_7 and R_8 are the same or different alkyl or alkenyl groups containing from 8 to 25 carbon atoms, and R_9 is hydrogen or C_1 - C_4 alkyl group and X^- is an anion, selected from a halide, methosulphate or ethosulphate,

(b) an alkoxyated dialkyl citrate as defined in claim 1 above, and

(c) one or more alkoxyates selected from:

(i) an alkyl fatty acid alkoxyate of the formula:

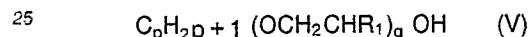


wherein R_{10} is a C_{11} - C_{19} alkyl or alkenyl group,

$\text{R}_1 = \text{H}$ or CH_3

m has a value from 1 to 6; and

(ii) an alkyl alkoxyate of the formula:



wherein p is an integer from 12-20, and

q has a value from 1 to 15; and optionally,

(d) an electrolyte.

7. A fabric softening formulation according to claim 6 wherein each of the substituents R_2 and R_3 in component (a) represent a substituent in which more than 50% of the groups are C_{16} and/or C_{18} alkyl and/or alkenyl groups.

8. A formulation according to claim 7 wherein each of the substituents R_2 and R_3 represent a mixture of 50-90% C_{18} alkyl or alkenyl groups and 10-50% C_{16} alkyl or alkenyl groups.

9. A formulation according to any one of the preceding claims 6-8 wherein the components (a), (b) and (c) are present in the following ranges by weight based on the total weight of the three components:

(a) 10 to 90%

(b) 5 to 60%

(c) 5 to 60%

10. A formulation according to any one of the preceding claims 6-9 wherein the components (a), (b) and (c) are dispersed as a preblend in water with moderate shearing at elevated temperature.

11. A formulation according to claim 10 wherein the total amount of the components (a), (b) and (c) in the water is from 2-10% by weight.

12. A formulation according to claim 1 wherein said formulation contains in addition to the alkoxydialkyl-citrate a smectite clay.



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	EP-A-0 159 920 (UNILEVER) * Examples; claims * ---	1	C 11 D 1/835 C 11 D 1/62 C 11 D 1/66
A	EP-A-0 122 141 (UNILIVER) * Examples; claims * ---	1	
A	EP-A-0 243 735 (HENKEL) * Claims; page 4, line 8 * ---	1	
A	EP-A-0 199 131 (RAFFINERIA OLII LUBRIFICANTI "R.O.L." S.p.A.) * Column 6, lines 1-12; claims * -----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 11 D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 26-06-1989	Examiner GOLLER P.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			