



**EUROPEAN PATENT APPLICATION**

Application number : **94302615.3**

Int. Cl.<sup>5</sup> : **C11D 1/37, C11D 1/06**

Date of filing : **13.04.94**

Priority : **15.04.93 GB 9307805**

Inventor : **Orlandini, Francesco Maurizio**  
**Research Laboratory,**  
**Olivier van Noortlaan 120**  
**NL-3133 AT Vlaardingen (NL)**

Date of publication of application :  
**19.10.94 Bulletin 94/42**

Representative : **Elliott, Peter William et al**  
**Unilever plc**  
**Patent Division**  
**Colworth House**  
**Sharnbrook**  
**Bedford MK44 1LQ (GB)**

Designated Contracting States :  
**AT BE CH DE DK ES FR GB GR IE IT LI NL PT**  
**SE**

Applicant : **UNILEVER PLC**  
**Unilever House**  
**Blackfriars**  
**London EC4P 4BQ (GB)**

**GB IE**

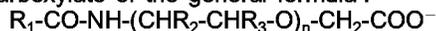
Applicant : **UNILEVER N.V.**  
**Weena 455**  
**NL-3013 AL Rotterdam (NL)**

**BE CH DE DK ES FR GR IT LI NL PT SE AT**

**Cleaning composition.**

Alkylamide polyethoxy carboxylate containing cleaning composition are significantly improved by the presence of magnesium ions. The invention provides a liquid, aqueous cleaning composition comprising :

a) an alkylamide polyethoxy carboxylate of the general formula :



wherein R<sub>1</sub> is C<sub>8</sub>-C<sub>18</sub> linear or branched alkyl, R<sub>2</sub> and R<sub>3</sub> are hydrogen or alkyl and n is 1-10, and,

b) at least 10 mole% magnesium ions based on the molarity of (a).

Field of the Invention

The present invention relates to a cleaning composition, particularly suitable for dishwashing.

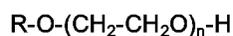
5 Background of the Invention

Commercial hand dishwashing compositions typically comprise, as the principal surfactant component, one or more surfactants selected from a relatively small group of components. In particular, principal surfactants are typically selected from amongst primary alcohol sulphates, secondary alkane sulphonates, linear alkyl benzene sulphonate, ethoxylated alcohols and alkyl ether sulphates.

In addition to these principal surfactants it is commonplace for compositions to comprise a so called 'foam-booster', selected from amine oxides, alkanolamides (particularly the mono and di ethanolamides and isopropanolamides) and other nitrogen-based surfactant compounds, including poly-hydroxy amides and betaines.

All of these compositions can suffer from stability problems if formulated incorrectly, particularly at low temperatures. As compositions frequently comprise several surfactant components there is no general rule for determining whether a particular composition will be stable or not. Formulations comprising monoethanolamide are particularly difficult to stabilise at a low temperature.

Many compositions are known which make use, as the principal surfactant, of ethoxylated alcohol nonionic surfactants of the general formula:



where R is alkyl and n is typically 5-14, or the related alkyl ether sulphates of the general formula:

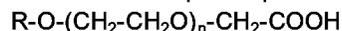


where R is again alkyl and n is typically 1-5.

In typical commercial formulations, some 80% of the surfactant system comprises ether sulphates, with the balance of the actives comprising one or more foam-boosters. The overall active concentration on product typically varies from around 20% for 'economy' brands to around 40% for 'concentrated' products.

Over many years, other surfactants have been proposed for use in hand dishwashing formulations and in cleaning compositions in general.

One such class are the carboxyl-terminated surfactants derived from fatty alcohols by interposing hydrophilic oxygen heteroatoms into the aliphatic chain of simple soaps. These molecules are of the general formula:



Where R is alkyl and n is typically 1-5.

Alkyl polyethoxy carboxylates obtained via the sodium hydroxide adduct of an ethoxylated alcohol, subsequently treated with chloracetic acid have been known for over twenty years: see 'Nonionic Surfactants' by M.J. Schick [1967: Marcel Dekker, LCCC 66-22492] pages 388-389.

The above-mentioned compounds are known to be very sensitive to the presence of calcium and magnesium ions, which form sparingly soluble salts with the surfactants, especially with the compounds having low degrees of ethoxylation. The formation of these salts adversely affects the performance of the surfactants.

WO 9208777 (P&G: November 1990): discloses the use of narrow EO range alkyl polyethoxy carboxylates in combination with 0.1-4% magnesium and/or calcium and a weak chelating agent for magnesium and/or calcium. The document suggests hand dishwashing formulations which contain 5-70% of a surfactant system comprising 80-100% of an alkyl polyethoxy carboxylates, up to 10% of an alcohol ethoxylate and up to 10% soaps.

Ethoxylation of fatty amides, rather than fatty alcohols, and subsequent treatment with chloracetic acid, leads to a distinct class of compounds of the general formula:



wherein R is alkyl and n is generally 1-10. Compounds having n=1 are known from DE Offenlegungsschrift 2644498. Compounds having n= 2-10 are disclosed in EP 0102118, as are synthetic methods for obtaining these compounds. EP 0236984 discloses the use of the above-mentioned compounds, as the alkali metal (preferably sodium), ammonium, substituted amine (preferably triethylamine) or magnesium salt in solid soap bars.

The above-mentioned compounds, known as the alkylamide polyethoxy carboxylates, have been proposed for use in hand dishwashing compositions by raw material suppliers, as the sodium salt.

The alkylamide polyethoxy carboxylate based dishwashing compositions disclosed in the above-mentioned literature are typically formulated at a pH of around 7.0 although formulations with pH up to 7.8 have been proposed. In typical formulations a relatively low level of alkylamide polyethoxy carboxylate is present, together with a relatively higher level of alkyl ether sulphate and/or alkane sulphonate.

Brief Description of the Invention

We have now determined that alkylamide polyethoxy carboxylate containing cleaning composition are significantly improved by the presence of magnesium ions.

5 Accordingly, the present invention provides a liquid, aqueous cleaning composition comprising:

a) an alkylamide polyethoxy carboxylate of the general formula:



wherein  $R_1$  is  $C_8$ - $C_{18}$  linear or branched alkyl,  $R_2$  and  $R_3$  are hydrogen or alkyl and  $n$  is 1-10, and,

b) at least 10 mole% magnesium ions based on the molarity of (a).

10

Detailed Description of the Invention

Typically, formulations according to the present invention comprise (a) and (b) in a molar ratio of from 9:1 to 1:10.

15 The magnesium can be present as a salt, preferably as the sulphate, in solution.

Generally, compositions according to the present invention will comprise alkylamide polyethoxy carboxylate in which the ethoxy blocks are unbranched.

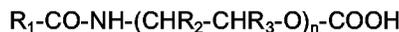
pH

20

We have also determined that the performance of the above-mentioned compositions can be further improved by formulation at a pH above 8.0.

Accordingly, preferred embodiments of the present invention comprise 0.01-70% of an alkylamide polyethoxy carboxylate of the general formula:

25



wherein  $R_1$  is  $C_8$ - $C_{18}$  linear or branched alkyl,  $R_2$  and  $R_3$  are hydrogen or alkyl and  $n$  is 1-10, said composition have a pH of from 8.0 to 11.0 and further comprise a magnesium salt.

As in the rest of this specification, all percentages are % weight on total product unless stated otherwise.

30

In preferred embodiments of the present invention the pH of the composition falls into the range 8-9.5, and is most preferably around 9.0.

This pH can be achieved by the use of a suitable buffering system such as an alkaline tetra borate or by the addition of a suitable alkali, preferably an alkali metal hydroxide.

Electrolyte

35

As mentioned above, magnesium is an essential component of the formulations according to the present invention.

Preferably, other electrolytes can be present at levels of 0.1-5% by weight of the overall composition. Particularly preferred amongst the electrolytes are alkali metal halides, carbonates, bicarbonates and sulphates.

40

The most preferred electrolyte is sodium chloride. Sodium chloride is conveniently present at a level of 0.1-5%, as a viscosity modifier.

Surfactants

45

As mentioned above, it is essential that at least one of the surfactant components of the compositions according to the present invention comprises an alkylamide polyethoxy carboxylate.

The total surfactant level in compositions according to the present invention may vary from around 5% to around 70% on product. Preferred formulations will typically comprise 15-25% or 35-45% active on product.

50

Preferred compositions according to the invention comprise an alkylamide polyethoxy carboxylate with a relatively narrow ethoxy chain length distribution. Preferably, the alkylamide polyethoxy carboxylate comprises low levels of the  $n=1$  compound. It is believed that, as compared with alkyl polyethoxy carboxylates the alkylamide polyethoxy carboxylates of the present invention have a narrower ethoxy chain length distribution and therefore comprise lower levels of the calcium sensitive low EO materials and lower levels of the less surface active high EO materials.

55

It is preferable that other surfactant components than the above-mentioned alkylamide polyethoxy carboxylates are present in compositions according to the invention.

Particularly suitable surfactant components can be selected from: secondary alkane sulphonates, fatty acid ester sulphonates, dialkyl sulphosuccinates, alpha-olefin sulphonates, primary alkyl sulphates, alkylben-

zene sulphonates, alkyl ether sulphates, betaines, amine oxides, ethoxylated alcohols, ethoxylated alkanolamides, ethoxylated alkylphenols, and ethoxylated fatty acid.

In preferred embodiments of the present invention the composition further comprises at least one anionic surfactant.

5 Preferably, the anionic surfactant is selected from alkyl sulphates, alkyl ester sulphonates and mixtures thereof.

The most preferred anionic surfactant is a linear alkyl ether sulphate of the general formula:



10 wherein  $R_1$  is straight or branched,  $C_8$  to  $C_{18}$  alkyl and the average degree of ethoxylation  $m$  is 1-14, more preferably 1-5, most preferably around 1.

The linear alkyl ether sulphates are mild, high-foaming anionic surfactants which are commercially available in quantity.

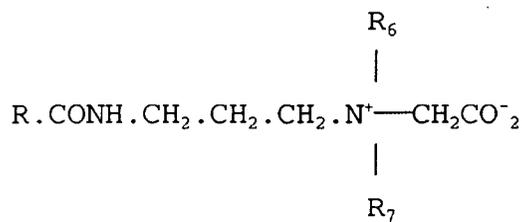
15 Preferred levels of anionic surfactant on product are to some extent determined by the total final concentration of actives in the product. For relatively dilute products levels of anionic preferably range from 13-18% whereas for more concentrated products levels of anionic range from 25-40%.

In preferred embodiments of the invention the composition further comprises a zwitterionic surfactant.

It is believed that the combination of zwitterionic surfactants, including betaines, with alkylamide polyethoxy carboxylates is a further unique feature of the present invention.

Preferred zwitterionic surfactants include amido betaines and alkyl betaines.

20 Preferred zwitterionic surfactants are amido betaines of the general formula:



30 wherein

R is straight or branched  $C_8$  to  $C_{18}$  alkyl,

$R_6$  is  $C_1$  to  $C_3$  alkyl or  $C_1$  to  $C_3$  hydroxyalkyl, and

35  $R_7$  is  $C_1$  to  $C_3$  alkyl or  $C_1$  to  $C_3$  hydroxyalkyl;

Preferred levels of zwitterionic surfactant on product are to some extent determined by the total final concentration of actives in the product. For relatively dilute products levels of zwitterionic preferably range from 1-4% whereas for more concentrated products levels of zwitterionic range from 3-9%.

It is preferable that both anionic and zwitterionic surfactant are present.

In particularly preferred embodiments of the present invention, the surfactant system comprises:

- 40 a) 100-200 parts by weight anionic surfactant,  
 b) 15-50 parts by weight of a zwitterionic surfactant, and,  
 c) 1-25 parts by weight alkylamide polyethoxy carboxylate.

In preferred embodiments of the invention the surfactant system further comprises a nonionic surfactant, most preferably an alcohol ethoxylate, glucamide, gluconamide, sulphoxide or lacto-bionamide.

45 In the most preferred embodiments of the present invention there is provided a liquid, aqueous, light duty cleaning composition comprising 10-50% on product of a surfactant system comprising:

- a) 100-200 parts by weight of an anionic surfactant selected from the group comprising alkyl sulphates, alkyl ester sulphonates and mixtures thereof,  
 b) 15-50 parts by weight of a betaine, and,  
 50 c) 1-25 parts by weight alkylamide polyethoxy carboxylate, and,  
 d) 1-10% on product of a water soluble magnesium salt.

### Minors

55 Among other, inessential, ingredients which may also be used in compositions according to the present invention are opacifiers (e.g. ethylene glycol distearate), thickeners (e.g., guar gum), antibacterial agents, anti-tarnish agents, weak metal chelators (e.g. citrates, glycinates), perfumes, abrasives (e.g. calcites and dolomites) and dyes. The use of strong metal chelating agents with a high affinity for magnesium is discouraged

as these will reduce the benefits associated with the presence of magnesium.

Compositions according to the present invention can further comprise a solvent, preferably, when present, at level of 1-15%wt on product, more preferably at a level of 2-7% on product.

5 Preferably, any solvent present is selected from: propylene glycol mono n-butyl ether, dipropylene glycol mono n-butyl ether, propylene glycol mono t-butyl ether, dipropylene glycol mono t-butyl ether, diethylene glycol hexyl ether, ethyl acetate, methanol, ethanol, isopropyl alcohol, ethylene glycol monobutyl ether, di-ethylene glycol monobutyl ether and mixtures thereof.

Most, preferably the solvent is a glycol ether or C<sub>2</sub>-C<sub>5</sub> alcohol solvent.

10 Particularly preferred solvents are selected from the group comprising ethanol (preferably as industrial methylated spirits), propylene glycol mono n-butyl ether (available as 'Dowanol PnB' [RTM]) and di-ethylene glycol monobutyl ether (available in the marketplace both as 'Butyl Digol' [RTM] or 'Butyl Carbitol' [RTM]).

A further inessential component is alkylene glycol, typically present at a level of 2-10% on product, irrespective of the overall surfactant concentration.

Propylene glycol is particularly suitable as a hydrotrope and/or viscosity modifier.

15 The present invention is further described with reference to the following non-limiting examples.

### EXAMPLES

20 In order to demonstrate the advantages of the present invention embodiments of the present invention and comparative formulations were subjected to identical 'plunger tests'. In these tests the products were dosed into water of 24 French hardness to a final concentration of 3 gr/l. The initial temperature of the water being 45°C.

Materials used in the comparative examples and embodiments are identified below:

25 LES: Lauryl ether sulphate, anionic surfactant, available in the marketplace as LIALET 123 1EO [RTM],

AAPB: Alkanamido propyl dimethyl betaine, zwitterionic surfactant, available in the marketplace as ANFO-DAC LB [RTM],

LMEA: Linear mono ethanolamide,

30 AAPC: Alkylamide polyethoxy carboxylate, available in the marketplace as AkypoSoft [RTM] KA 250 BY ex CHEM-Y.

### EXAMPLES 1-4

35 Examples 1-4 illustrate the effects of the presence and absence of magnesium ions at the conventional Ph and at a higher pH. Results of a series of evaluations are given in Table 1 below. Magnesium was added as the sulphate. Examples 1/2 and 3/4 are paired comparisons performed at the same time.

40

45

50

55

TABLE 1

EXAMPLE	1	2	3	4
COMPONENT:				
ACTIVES:				
By Parts:				
LES	80	80	80	80
AAPB	15	15	15	15
LMEA	-	-	-	-
AAPC	5	5	5	5
By Percent:				
ACTIVES:	19.5	19.5	19.5	19.5
Mg <sup>2+</sup>	-	-	0.35%	0.35%
water	-----to 100%-----			
pH	9	7	9	7
foam volume:	9610	11805	14030	12910

From the results given in Table 1 it can be seen that foaming behaviour of the formulations given in comparative examples 1 and 2 were both improved by the addition of magnesium, as in embodiments illustrated by examples 3 and 4. It can also be seen that the embodiment illustrated by examples 4 was further improved as regards foam volume by formulation at a pH of 9.0 as opposed to the conventional pH of 7.0 formulation. By comparing the effects of pH in the magnesium free formulations given in comparative examples 1 and 2 it can be seen that the improvement associated with an increase in pH is not achieved in the absence of magnesium.

#### EXAMPLES 5-10

Examples 5-10 illustrate the effects of varying the levels of magnesium ions in paired comparison tests of which the results are given in examples 5/6, 7/8 and 9/10 respectively. Results are given in Table 2 below.

TABLE 2

EXAMPLE	5	6	7	8	9	10
ACTIVES:						
By Parts:						
LES	80	80	80	80	80	80
AAPB	15	15	15	15	15	15
LMEA	-	-	-	-	-	-
AAPC	5	5	5	5	5	5
By percent:						
ACT:	19.5	19.5	19.5	19.5	19.5	19.5
Mg <sup>2+</sup>	-	0.35	-	0.47	-	0.70
water	-----to 100%-----					
fv:	10430	12275	9885	10335	12010	12515

From the above results it can be seen that the addition of magnesium improved the foam volume (fv) in all cases. Compositions according to examples 6, 8 and 10 were stored at both ambient temperature and at a temperature below 0°C. In all cases the compositions showed no phase separation after storage.

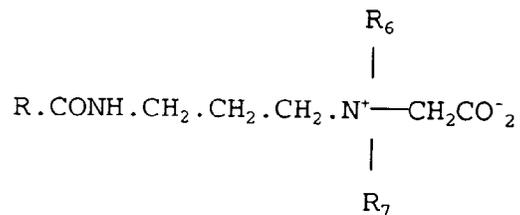
### Claims

- An aqueous cleaning composition comprising:
  - an alkylamide polyethoxy carboxylate of the general formula:  

$$R_1\text{-CO-NH-(CHR}_2\text{-CHR}_3\text{-O)}_n\text{-CH}_2\text{-COO}^-$$
 wherein R<sub>1</sub> is C<sub>8</sub>-C<sub>18</sub> linear or branched alkyl, R<sub>2</sub> and R<sub>3</sub> are hydrogen or alkyl and n is 1-10, and,
    - at least 10 mole% magnesium ions based on the molarity of (a).
- Composition according to claim 1 comprising (a) and (b) in a molar ratio of from 9:1 to 1:10.
- Composition according to claim 1 having a pH of from 8.0 to 11.0.
- Composition according to claim 1 comprising 15-45% total surfactant on product.
- Composition according to claim 1 further comprising at least one anionic surfactant other than alkylamide polyethoxy carboxylate.
- Composition according to claim 5 comprising a linear alkyl ether sulphate of the general formula:  

$$R_1\text{-(OCH}_2\text{CH}_2)_m\text{-SO}_3^-$$
 wherein R<sub>1</sub> is straight or branched, C<sub>8</sub> to C<sub>18</sub> alkyl and the average degree of ethoxylation m is 1-14.
- Composition according to claim 1 further comprising at least one zwitterionic surfactant.
- Composition according to claim 7 comprising an amido betaine of the general formula:

5



10

wherein

R is straight or branched C<sub>8</sub> to C<sub>18</sub> alkyl,  
R<sub>6</sub> is C<sub>1</sub> to C<sub>3</sub> alkyl or C<sub>1</sub> to C<sub>3</sub> hydroxyalkyl, and  
R<sub>7</sub> is C<sub>1</sub> to C<sub>3</sub> alkyl or C<sub>1</sub> to C<sub>3</sub> hydroxyalkyl.

15

9. Composition according to claim 1 wherein the surfactant system comprises:

- a) 100-200 parts by weight anionic surfactant,
- b) 15-50 parts by weight of a zwitterionic surfactant, and,
- c) 1-25 parts by weight alkylamide polyethoxy carboxylate, and,
- d) 1-10% on product of a water soluble magnesium salt.

20

10. Composition according to claim 1 further comprising a nonionic surfactant.

25

30

35

40

45

50

55



European Patent  
Office

EUROPEAN SEARCH REPORT

Application Number

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 94302615.3
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	<p><u>EP - A - 0 215 504</u> (STAMICARBON B.V.) * Claims *</p> <p style="text-align: center;">--</p>	1, 5, 6	<p>C 11 D 1/37 C 11 D 1/06</p>
X, D	<p><u>EP - A - 0 102 118</u> (CHEM-Y FABRIK VAN CHEMISCHE PRODUKTEN B.V.) * Claim 6; page 2, lines 9-17 *</p> <p style="text-align: center;">----</p>	1, 5, 6	
			<p><b>TECHNICAL FIELDS SEARCHED (Int. Cl.5)</b></p> <p>C 11 D</p>
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 22-07-1994	Examiner SEIRAFI
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>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</p>		<p>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</p> <p>..... &amp; : member of the same patent family, corresponding document</p>	

EPO FORM 1503 03/82 (P0401)