

11) Publication number:

0 162 600

A1

(12)

## **EUROPEAN PATENT APPLICATION**

(21) Application number: 85302875.1

(51) Int. Cl.<sup>4</sup>: **C** 11 **D** 1/88 **C** 11 **D** 1/94

22 Date of filing: 24.04.85

30 Priority: 25.04.84 GB 8410501

(43) Date of publication of application: 27.11.85 Bulletin 85/48

Designated Contracting States:
 AT BE CH DE FR GB IT LI LU NL SE

(71) Applicant: Fishlock-Lomax, Eric Graham
Douglas House
Chipping Warden Nr. Banbury Oxfordshire(GB)

(2) Inventor: Fishlock-Lomax, Eric Graham
Douglas House
Chipping Warden Nr. Banbury Oxfordshire(GB)

(74) Representative: Skailes, Humphrey John et al, Frank B. Dehn & Co. Imperial House 15-19 Kingsway London WC2B 6UZ(GB)

<sup>(54)</sup> Cleaning compositions.

<sup>(5)</sup> Cleaning compositions (particularly liquid water-based compositions such as liquid detergents and hard surface cleaners) are described which contain at least two principal amphoteric surfactants and at least one non-ionic surfactant. One of the two amphoteric surfactants is of the acylamino type and the other is of the alkylamino or alkoxypropylamino type.

EL147-473

#### CLEANING COMPOSITIONS

This invention concerns compositions for cleaning a wide range of items including hard surfaces and soft goods such as textiles both for commercial and home use.

The invention is primarily concerned with liquid water-based cleaning compositions such as liquid detergents, carpet cleaners, dishwashing liquids and hard surface cleaners, but the same principles are equally applicable to solid compositions for example in powder form.

10 Prior to this invention various suggestions have been made for obtaining synergistic detergency between one amphoteric and one or more nonionic surfactants. To my surprise I have found considerable further benefits of synergistic detergency, low temperature cleaning, and improved compatibility characteristics by using more than one principal (cleaning) amphoteric surfactant with at least

The invention thus provides a cleaning compostion 20 (preferably in liquid water-based form) which comprises at least two amphoteric surfactants and at least one non-ionic surfactant.

These compositions offer many advantages including particular:

25 a) Improved detergency at low concentrations and low cost

one non-ionic surfactant.

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- b) Very wide applicability to various cleaning uses
- c) Outstanding detergency at low temperatures with consequent energy saving
  - d) Ability to produce highly concentrated liquid detergent compositions even in the presence of alkaline builder

with many types of additives normally used in detergent compositions to confer specific additional properties.

Depending on the intended use, the compositions 5 may also contain additives conventionally included in cleaning formulations. For example other surfactant may be added for specific properties, for examples to add bactericidal properties, to boost foam or to confer softening properties. A further feature 10 of this invention is the ease of incorporation of such additional surfactants without problems such as surfactant compatibility and stability of the formulation. Other additives may include alkaline builders to improve detergency, chelating 15 or sequestering agents to avoid problems with heavy metal ions, optical brightening agents, solvents, dyes and perfumes.

The amphoteric surfactants may be of the 20 type having the general formula (I)

$$R-(CO)_z - (OCH_2CH_2CH_2)_n - (N-(CHR^1)_x)_y - N-Q$$
 $B$ 
(I)

25 where R is a  $C_{8-20}$  hydrocarbyl group, optionally substituted;

 $R^1$  is H or  $C_{1-6}$  alkyl;

B is H, alkyl or substituted alkyl, or a group Q as defined below;

Q is an anionic moiety;

x is 2 to 6:

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y is 0 to 5;

z to 0 or 1; and

n is 0 or 1 (z being 0 when n is 1).

The compositions generally contain one or more (first) amphoteric surfactant(s) in which z is 0 and preferably one or more (second) amphoteric surfactant(s) in which z is 1.

In these compounds, R may for example be a straight or branched alkyl or alkenyl group; a or cycloalkyl-alkyl (e.g. cyclohexyl-alkyl) group; an aralkyl or aralkenyl group in which the alkyl or alkenyl portion contains at least 6 carbon atoms; or the hydrocarbyl portion of a resinic acid containing at least two fused rings, e.g. as in the tricyclic pine resin acids such as abietic acid.

R is preferably a C<sub>10-16</sub> alkyl group, e.g.

10 a C<sub>12</sub> group and an example of a branched chain group is C<sub>16</sub>H<sub>33</sub>CH(CH<sub>3</sub>)-. The aliphatic portion of R may for example be the hydrocarbyl portion of lauric or coconut fatty acid, both of which contain high portion of C<sub>12</sub> constituents. An example of an unsaturated R group is oleyl. R may for example be substituted by hydroxy, as in hydroxystearyl, or by -COOH (e.g. at the 2- position).

In most surfactants of the formula(1) type, n is 0.

20 R<sup>1</sup> is usually a hydrogen atom, but may be an alkyl group such as methyl.

When B is an alkyl group, it may have 1 6, preferably 2 - 4, carbon atoms, and is preferably a straight chain group. Examples of such groups

25 are methyl and ethyl. The alkyl group may be substituted, for example by hydroxy, as 2-hydroxyethyl, or by amino.

The group Q may for example be of the formula  $-R^2COOM$  where  $R^2$  is a  $C_{1-6}$  alkylene group (such as methylene or ethylene) and M is hydrogen or an alkali metal, alkaline earth metal, ammonium or substituted ammonium ion (e.g. mono-, di- or tri-hydroxyethylammonium). M is preferably sodium, and  $R^2$  is preferably methylene.

For the purposes of this invention, and because of the change of ionic properties with pH shown by amphoteric surfactants, the free -COOH group

is considered equivalent to -COONa or -COOK and sammorium or amine or other carboxylic acid salts.

The composition of this invention preferably contains a first amphoteric surfactant of formula

(1) where R is a C<sub>8-20</sub> hydrocarbyl group derived from coco or tallow fatty acids;

R<sup>1</sup> is H,

B is H or Q as defined below

Q is an anionic moiety, preferably CH<sub>2</sub>COONa or

 $10 - {}_{2}CH_{2}CH_{2}COONa$ ,

x is 2 to 4,

y is 0 to 4,

z is 0, and

n is 0;

in combination with a second amphoteric surfactant of formula (I) where:

R is a  $C_{8-20}$  hydrocarbyl group derived from coco, oleic or tall oil fatty acid,  $R^1$  is H,

20 B is H, hydroxyethyl or a group Q as defined below, Q is an anionic moeity, preferably CH<sub>2</sub>COONa or CH<sub>2</sub>CH<sub>2</sub>COONa,

x is 2,

y is l,

25 z is 1, and

n is 0.

Commercially available examples of the first amphoteric surfactant include Deriphat 151, Deriphat-154, and the full sodium salts of Deriphat 151C,

30 Deriphat 161C, Amphoram CP1, Diamphoram CP1, Triamphoram CP1, and Polyamphoram CP1 and Ampholak QTE (Deriphats available from Henkel, Amphorams from Ceca and Ampholak QTE from Amphoterics International Ltd.).

Commercially available examples of the second

amphoteric surfactant include products classed

as cocoamphoglycinate or cocoamphopropionate (and

similar products made from the other fatty acids

listed), or cocamphocarboxyglycinate or cocoamphocarboxy-

propionate (and similar products made from the other fatty acids listed), for example Miranol CM, C2M or C2MSF.

In general the relative (weight) concentrations
of the two amphoteric surfactants used is from
90:10 to 10:90, preferably 3:1 to 2:1 (first amphoteric:
second amphoteric).

The non-ionic surfactants used are preferably ethylene oxide or propylene oxide/ethylene oxide

10 adducts of alkylphenols (e.g. nonylphenol) or long chain alcohols or alkylamines (e.g. C<sub>12-14</sub> alcohols or C<sub>12-18</sub> alkylamines). The weight ratio of the principal amphoteric surfactants to the non-ionic surfactant(s) is generally from 10:1 to 1:2, preferably from 2.5:1 to 1.5:1 (e.g. about 2:1).

The non-ionic surfactant may for example
be a nonylphenol-ethylene oxide adduct containing
6 -12 moles ethylene oxide, a C<sub>12-14</sub> alcohol-ethylene
oxide adduct containing 7 - 10 moles ethylene oxide,
20 a C<sub>12-18</sub> alkylamine-ethylene oxide adduct containing
7 - 15 moles ethylene oxide or an equivalent ethylene
oxide/propylene oxide block copolymer adduct.

When a second non-ionic surfactant is included, it is may be of the same general type but is preferably 25 more lipophilic than the main non-ionic surfactant. The second material may for example be a nonylphenolethylene oxide adduct containing 4 - 6 moles ethylene oxide, a C<sub>12-14</sub> alcohol-ethylene oxide adduct containing 4 - 6 moles ethylene oxide, a C<sub>12-18</sub> alkylamine— ethylene oxide adduct containing 2 - 5 moles ethylene oxide or an equivalent ethylene oxide/propylene oxide block copolymer adduct. A second non-ionic surfactant of this kind is generally used at a lower concentration than the first; for example, the weight ratio of the first to second surfactants may generally be from 100:1 to 60:40 or 70:30 in compositions containing a builder.

that the choice of non-ionic surfactant is not as critical as in conventional detergent systems, for example as regards the balance of detergent properties and water solubility required particularly in built systems. The amphoteric surfactants also solubilise the non-ionic surfactants in formulations containing a builder.

The compositions may also contain, depending 10 on the intended use, additives such as builders (e.q. sodium metasilicate (anhydrous or pentahydrate), tetrapotassium pyrophosphate, caustic soda or nitrilotriacetic acid), chelating or sequestering agents (e.g. trisodium nitrilotriacetic acid, tetrasodium 15 ethylenediamine tetracetic acid and trisodium hydroxyethylethylenediamine triacetic acid), solvents (e.g. glycolethers such as butyl glycol ether, butyl cellosolve), fabric conditioners (e.g. quaternary ammonium salts, such as a di-fatty (usually tallow) 20 dimethylammonium chloride (e.g. Arquad 2 HT) or a di-fatty (usually tallow) imidazoline methosulphate or ethosulphate quaternary salt (e.g. Ammonyx 4080 (Millmaster-Onyx), Imisoft 75 (M & S Chemicals) & Ampholak TO (Amphoterics International)), foam 25 boosters (such as alkyl betaines or amine oxides, e.g. Emigen BB & BT, Aromox DMDC (Akzo) and Empigen OB (Albright & Wilson), Ammonyx LO and CDO (Millmaster-Onyx)), bactericides (e.g. a bactericidal surfactant such as a benzalkonium chloride (e.g. Imiquat BKC) 30 or BTC 2125), optical brighteners (e.g. Tinopal CBS-X & Tinopal 5BMS-X (Ciba)), dyes and perfumes.

The quantity of such additives used will vary according to the application and the nature of the particular additive. In general however liquid systems may contain 1-40% of a builder, 1-20% chelating agent, 1-10% solvent, 1-5% fabric conditioner, 1-5% foam booster, 1-5% bactericide, 0.1-1% optical brightener and 0.1-1% dyes and /or

perfumes (percentages herein are by weight unless otherwise stated).

Liquid compositions which do not contain a builder may for example contain up to 50 % of the principal amphoteric surfactants and up to 25 % non-ionic surfactants, e.g. up to 40% first amphoteric surfactant, up to 10% second amphoteric surfactant, up to 20% first non-ionic surfactant and up to 5% second non-ionic surfactant.

(Percentages given herein for the amphoteric and non-ionic surfactants are on the basis of 30% active for the amphoterics and 100% active for the non-ionics; 'active' refers to concentration relative to the undiluted material).

Liquids detergents of the invention may for example have the following compositions:

	General	Preferred
First amphoteric	10-25%	18-22%
Second amphoteric	2-6%	3 <b>-</b> 5%
Non-ionic surfactant(s)	3-15%	8-12%
Builder	1-40%	10-20%
Chelating agent	1-20%	5-10%
Fabric conditioner	1-5%	2-4%
Optical brightener	0.1-1%	0.2-0.6%
Dye, perfume	0.1%-1%	0.2-0.6%
Water	to 100%	

It will be appreciated that the overall compositions can be varied widely within the above ranges. The preferred concentration ranges refer to compositions of conventional dilution, but one of the advantages of the invention is that it offers the possibility of very highly concentrated solutions. Such compositions may for example contain up to 35% (e.g. 20-35%) of the builder (e.g. sodium metasilicate), up to 90% (e.g. 10-50%) of the two principal amphoteric

15% of the second type) and up to 15% (e.g. 3-15%) of non-ionic surfactant(s). Examples of such compositions are

~ :

	Builder	First	Second	Non-ionic	Water
5		Amphoteric	Amphoteric		
	30%	9%	1%	3%	57%
	25%	17%	5%	8%	46%
	22%	23%	4%	11%	40%

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Hard surface cleaners of the invention may for example have the following composition:

		General	Preferred
15			
	Amphoteric - 1	2-8%	3-5%
	Amphoteric - 2	1-4%	1.5-2.5%
	Non-ionic surfactant(s)	1-6%	2-4%
20	Solvent	1-5%	2-4%
	Builder	0-15%	8-12%
-	Foam booster	1-5%	2-4%
	Bactericide	1-5%	2-4%
	Water	to 100%	

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The following examples illustrate the invention. Example 1

A hard surface cleaner was made using 4% of the first type of amphoteric (Ampolak YCE),

30 2% of the second type of amphoteric (e.g. cocoamphoglycinate) together with 2% nonyl phenol 9 mole ethoxylate and 1% nonyl phenol 5.5 mole ethoxylate. This basic surfactant composition together with builders such as sodium metasilicate pentahydrate

35 or tetra potassium pyrophosphate (10%) gave excellent cleaning results. Furthermore it was found possible to incorporate a bactericide of the 'benzalkonium chloride' type (3%) as well as a solvent such as

butyl glycol ether (3%). Higher concentrations of the same type of formulation were easily possible without loss of stability. The results obtained were such as to give considerably better performance that conventional hard surface cleaners.

3-5% of amine oxide and about 2% NaCl was also found useful to increase the viscosity of this formulation, as well as increasing flash foam.

Furthermore, such products are normally based

10 on anionic and nonionic surfactants where inclusion
of a cationic bactericide gives problems of compatibility.
Also, the amount of alkaline electrolyte which
can be included in conventional products is limited
by the level of surfactant (and vice versa). In

15 such cases the addition of hydrotrope such as sodium
xylene sulphonate is necesary in substantial amounts
to confer stability.

## Example 2

A liquid laundry detergent was prepared using,
20 as base surfactant composition, 16% of the first
type of amphoteric and 4% of the second type of
amphoteric (as in Example 1) together with 8% nonyl
phenol 9 mole ethoxylate and 2% nonyl phenol 5.5
mole ethoxylate. This was formulated with 15%
25 sodium metasilicate pentahydrate, 2% chelating
agent (sodium nitrilotriacetic acid), and optional
brighteners (0.4%), dye and perfume.

Washing at 30°C, or even 20°C, gave superior results as compared to both to a conventional type of liquid laundry detergent based on anionic and nonionic surfactants and also conventional powder detergents, both as regards detergency and whitening. Furthermore, because of the compatibility of the surfactant system described in this invention, it was found possible to include easily a cationic bactericide of the type mentioned above and also a cationic fabric conditioning product (3% Ampholak TQ, described as a di-fatty imidazoline quaternary).

Since the amphoteric surfactants used were calculated to be 30% active, the net active content of the surfactant base described was only about one quarter of the active content of the comparative 5 conventional laundry detergent and functioned better when used at only half the dosage level of the latter under the same conditions.

It was also found possible to prepare the compositions of Example 2 in more concentrated form, containing for example up to and over twice the stated concentrations of the various ingredients.

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Furthermore, it is well known that conventional liquid laundry detergents of about 40% active surfactant content and above require the addition of solubiliser or hydrotrope to confer stability and the addition 15 of alkaline builder to such a system is virtually impossible without total loss of stability. type of formulation described in this invention, however, provided a considerably better performing detergent composition into which alkaline builder was easily included.

By use of combinations of two types of amphoteric surfactant together with one or more nonionic surfactants it was found possible to obtain excellent detergency 25 even at low temperature coupled with ease of incorporation into alkaline 'built' products and with greater flexibility regarding the possible incorporation of useful cationic additives. Not only does this offer better performance at lower cost but further 30 savings are possible by omission of otherwise nonfunctional ingredients such as solubilisers and hydrotropes. Such is the ease of formulation with this system that it is possible to produce highly concentrated products or combinations of products, 35 thus reducing the weight and volume of product for a given purpose, reducing the amount of water needed in such products and thus offering cheaper packaging costs, and offering energy saving by possible use at lower temperatures.

#### CLAIMS

1. A cleaning composition which comprises at least two amphoteric surfactants and at least one non-ionic surfactant, of the type having the general formula (I)

$$R-(CO)_z - (OCH_2CH_2CH_2)_n - (N-(CHR^1)_x)_y - N-Q$$
 (I)

10

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where R is a  $C_{8-20}$  hydrocarbyl group, optionally substituted;

 $R^1$  is H or  $C_{1-6}$  alkyl;

B is H, alkyl or substituted alkyl, or a

group Q as defined below;

Q is an anionic moiety;

x is 2 to 6;

y is 0 to 5;

z to 0 or 1; and

n is 0 or 1 (z being 0 when n is 1); the composition containing at least a first amphoteric surfactant as defined above in which z is 0.

2. A composition according to claim 1 which contains a first amphoteric surfactant in which

25 z is 0 and a second in which z is 1.

3. A composition according to claim 1 which contains a first amphoteric surfactant of formula (1) where R is a  $C_{8-20}$  hydrocarbyl group derived from coco or tallow fatty acids;

30 R<sup>1</sup> is H.

B is H or Q as defined below

.Q is -CH2COONa or -CH2CH2COONa,

x is 2 to 4,

y is 0 to 4,

35 z is 0, and

n is 0;

in combination with a second amphoteric surfactant of formula (I) where:

R is a  $C_{8-20}$  hydrocarbyl group derived from coco, oleic or tall oil fatty acid,  $R^{1}$  is H,

B is H, hydroxyethyl or a group Q as defined below,

- 5 Q is  $-CH_2COONa$  or  $CH_2CH_2COONa$ ,
  - x is 2,
  - y is 1,
  - z is 1, and
  - n is 0.

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- 10 4. A composition according to claim 1 which contains two non-ionic surfactants, the second of which is more lipophilic than the first and is present at a lower concentration than the first.
  - 5. A composition according to claim 1 in which the weight ratio of the first amphoteric surfactant to the second amphoteric surfactant is from 3:1
  - to 2:1 and the weight ratio of the first and second amphoteric surfactants to the non-ionic surfactant(s) is from 2.5:1 to 1.5:1.
- 20 6. A composition according to claim 1 which contains one or more builders, chelating or sequestering agents, solvents, fabric conditioners, foam boosters, bactericides, optical brightners, dyes or perfumes as additives.
- 7. A composition according to claim 1 in the form of a liquid water-based composition.
  - 8. A composition according to claim 1 in the form of a liquid detergent having the composition A or B below, by weight:

30		<u>A</u>	<u>B</u>
	First amphoteric	10-25%	18-22%
	Second amphoteric	2-6%	3-5%
	Non-ionic surfactant(s)	3-15%	8-12%
	Builder	1-40%	10-20%
35	Chelating agent	1-20%	5-10%
	Fabric conditioner	1-5%	2-4%
	Optical brightener	0.1-1%	0.2-0.6%
	Dye, perfume	0.1%-1%	0.2-0.6%
	Water	to 100%	

- 9. A composition according to claim 1 in the form of a highly concentrated liquid detergent containing 10-50% of the first and second amphoteric surfactants, 3-15% of the non-ionic surfactant(s) and 20-35% of the builder, by weight.
- 5 10. A composition according to claim 1 in the form of a hard surface cleaner having the composition A or B below, by weight

	<u>A</u>	<u>B</u>	
10			
	First amphoteric	2-8%	3-5%
	Second amphoteric	1-4%	1.5-2.5%
	Non-ionic surfactant(s)	1-6%	2-4%
	Solvent	1-5%	2-4%
15	Builder	0-15%	8-12%
	Foam booster	1-5%	2-4%
	Bactericide	1-5%	2-4%
	Water	to 100%	



# **EUROPEAN SEARCH REPORT**

Application number

EP 85 30 2875

	Citation of document with indication, where of relevant passages					CLASSIFICATION OF THE APPLICATION (Int. Cl.4)	
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