



<sup>(1)</sup> Publication number:

0 520 551 A2

# (2) EUROPEAN PATENT APPLICATION

②1 Application number: 92201753.8 ⑤1 Int. Cl.<sup>5</sup>: **C11D** 1/83, C11D 3/20

2 Date of filing: 16.06.92

30 Priority: 28.06.91 GB 9114045

43 Date of publication of application: 30.12.92 Bulletin 92/53

Designated Contracting States:
CH DE ES FR GB IT LI NL SE

Output

Designated Contracting States:

Output

Designated Cont

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

& CH DE ES FR IT LI NL SE

7) Applicant: UNILEVER PLC
Unilever House Blackfriars P.O. Box 68
London EC4P 4BO(GB)

⊗ GB

Inventor: Thompson, Ian Divisione LEVER, via Lever Gibbs I-20071 Casalpusterlengo (Milan)(IT)

Representative: Kan, Jacob Hendrik, Dr. Unilever N.V. Patent Division P.O. Box 137 NL-3130 AC Vlaardingen(NL)

54) Liquid detegent compositions.

© A pearlescent liquid detergent composition comprises an organic pearlescer, at least 5% by weight of a primary alkyl sulphate anionic surfactant and less than 2.5% by weight of a pearlescer crystallisation enhancer selected from acids, salts, alcohols and esters having a hydrophobic moiety with an average of at least 16 carbon atoms and nonionic surfactants.

The present invention relates to liquid detergent compositions, more especially to those which have a pearlescent appearance.

It is well known to endow a pearlescent appearance to surfactant based-products so that they may convey an aesthetic appeal to the consumer. This is done quite often with cosmetic products such as shampoos. However, it is also sometimes done with products associated with the cleaning of fabrics, for example rinse conditioners, when it is desired to convey an impression of gentleness and care for the fabrics.

For the formulation of so-called light duty liquids (sometimes called fine wash liquids), ie liquid products for washing delicate fabrics such as woolens, eg by hand, it is known to use significant concentrations of alkylbenzene sulphonates (ABS) in the liquid product. Recent concerns about possible detrimental effects of ABS on the environment have lead to a desire to minimise the amount of ABS in such formulations. One alternative anionic surfactant which might be a suitable replacement for at least part of the ABS is a primary alkyl sulphate (PAS) surfactant.

There are several possible ways of making such a composition pearlescent. One way is to incorporate small mica crystals. However, to keep these crystals dispersed in the product, it is necessary to formulate it to have good solid-suspending properties. If the liquid is to remain pourable whilst being able to suspend solids, then it needs to have a suitable liquid crystalline phase. That in turn necessitates using relatively high concentrations of detergent active materials (surfactants) and usually also, relatively high concentrations of electrolytes. Such concentrated formulations tend to be unduly harsh for use with delicate fabrics.

Therefore, for light duty products it is necessary to use a long-chain organic pearlescer which can be crystallised-out in the formulation to give a good dispersion of crystals of the appropriate size and shape. Examples of such pearlescers are ethylene glycol monostearate and the corresponding distearate. Unfortunately, when used in products containing significant amounts of PAS, the crystallisation process yields poor crystals which give an inadequate pearlescent effect.

Thus, there is a problem in providing a pearlescent effect using the organic pearlescers in liquid compositions which contain reasonable quantities of PAS. Surprisingly, the applicants have found that this problem can be overcome by using a small amount of ABS or similar long-chain material or a nonionic surfactant in the formulation as well. Since a primary reason for using PAS is to minimise the amount of ABS used, clearly not too much of the latter should be used.

25

30

50

55

Thus the present invention provides a pearlescent liquid detergent composition comprising an organic pearlescer, at least 5% by weight of a primary alkyl sulphate anionic surfactant and less than 2.5% by weight of a pearlescer crystallisation enhancer which is an acid, salt or alcohol having a hydrophobic moiety with an average of at least 16 carbon atoms or a nonionic surfactant.

The hydrophobic moiety in the crystallisation enhancer may for example be an alkyl group, an alkenyl group or an alkylbenzene group. In the latter case, the atoms of the benzene ring are to be taken into account in the at least 16 carbon atoms. The alkyl groups or alkenyl group may optionally be alkoxylated with one or more alkoxy and/or propoxy groups. The acid group may be chosen from a wide class including the sulphates, sulphonates and carboxylates, preferably sulphonates and carboxylates.

Another preferred class of pearlescer crystallisation enhancers comprises the soaps. These are usually salts of alkali metals with fatty acids of appropriate chain length. It is convenient to provide a soap by reaction in situ, ie by incorporating both an appropriate alkali metal hydroxide and a fatty acid into the composition. Suitable fatty acids include oleic acid, ricinoleic acid and fatty acids derived from castor oil, rapeseed oil, groundnut oil, palmkernel oil or mixtures thereof. The sodium or potassium soaps of these acids are preferred.

It is especially preferred to incorporate two or more pearlescer crystallisation enhancers of different types, for example an alkylbenzene sulphonate and a soap.

The salts of the free acids are preferably the alkali metal, eg sodium or potassium, or alkaline earth metal salts. Such salts may be added in the salt form <u>per se</u> or formed <u>in situ</u> in the composition, eg by reaction with the appropriate metal hydroxide. It will be appreciated that many crystallisation enhancers are anionic or nonionic surfactants (vide infra).

In general, it is preferred that the hydrophobic moiety comprises on average at least about 18 carbon atoms. Some preferred crystallisation enhancers are sodium  $C_{11}$ - $C_{15}$ ) alkyl benzene sulphonates, stearic acid, sodium stearate, oleic acid and sodium oleate.

A further group of pearlescent enhancers according to the invention are the nonionic surfactants.

Although the amount of crystallisation enhancer must be less than 2.5% by weight of the total composition, preferably it is present at from 0.005% to 1.5% by weight, especially from 0.01% to 1%.

Any organic pearlescer may be used in compositions according to the present invention. Many examples will be known to persons skilled in the art but typical examples are ethylene glycol monostearate

and ethylene glycol distearate. Normally, only relatively small amounts of pearlescer need to be incorporated to produce the desired pearlescent appearance, for example from 0.1% to 5% by weight of the total composition, more especially from 0.5% to 2.5%.

Preferably, the primary alkyl sulphate has an average at from 8 to 15 carbon atoms, most preferably from 12 to 13. Although the amount of the primary alkyl sulphate constitutes at least 5% by weight of the total composition, preferably it is present from 10% to 20% by weight.

Compositions formulated according to the requirements defined in respect of the present invention are generally suited as light duty liquids for washing delicate fabrics. Therefore it is very much preferred to formulate them as aqueous compositions, especially as isotropic aqueous compositions. To this end, a small amount of hydrotrope may be incorporated, for example a low molecular weight alcohol.

The compositions of the present invention may also comprise a thickener, for example a polymer such as a suitable acrylate, methacrylate (or co-polymer thereof) or a cellulose such as hydroxymethyl cellulose. Typical inclusion levels of thickener are from 0.1% to 10%, eg from 0.5% to 5% by weight of the total composition.

It is also preferred that for light duty compositions, the concentration of detergent actives (soaps and non-soap surfactants) is not too high. For example, the amount of actives may be from 10% to 30% by weight of the total composition, most preferably from 15% to 25%.

15

55

Conversely, the amount of water will be relatively high, for example from 65% to 85%, most preferably from 70% to 80% by weight of the total compositions.

Many examples of such light duty compositions will be substantially free from inorganic detergency builders. However, whether or not a soap is incorporated as a pearlescer crystallisation enhancer, soaps may be included for other purposes. They may be regarded as surfactants, fabric softeners or detergency builders since they demonstrate all of these properties to a degree. In this capacity, soaps will usually be incorporated in small amounts, for example from 0.5% to 2.5% by weight of the total composition. Soaps included for these purposes may also be soaps of shorter chain-length fatty acids such as that derived from coconut oil. They may be incorporated as soap per se or formed in situ.

As well as the crystallisation enhancer and the primary alkyl sulphate, it is also possible to include other anionic non-soap surfactants in compositions according to the present inventions. The non-soap anionic surfactants as a class (including any chosen as crystallisation enhancers) are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher acyl radicals. Examples of suitable synthetic anionic detergent compounds other than those already mentioned are sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum; sodium coconut oil fatty monoglyceride sulphates and sulphonates; sodium and potassium salts of sulphuric acid esters of higher (C<sub>8</sub>-C<sub>18</sub>) fatty alcohol-alkylene oxide, particularly ethylene oxide, reaction products; the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid and neutralised with sodium hydroxide; sodium and potassium salts or fatty acid amides of methyl taurine; alkane monosulphonates such as those derived by reacting alphaolefin (C<sub>8</sub>-C<sub>20</sub>) with sodium bisulphite and those derived from reacting paraffins with SO<sub>2</sub> and Cl<sub>2</sub> and then hydrolysing with a base to produce a random sulphonate; and olefin sulphonates, which term is used to describe the material made by reacting olefins, particularly C<sub>10</sub>-C<sub>20</sub> alpha-olefins, with SO<sub>3</sub> and then neutralising and hydrolysing the reaction product.

It is also preferred to include a nonionic surfactant in the composition. Where the crystallisation enhancer is nonionic in character, it is still preferred to include additional nonionic surfactant for its detergency properties. The amount of nonionic surfactant included for detergency is preferably from 1% by weight to 15% by weight of the total composition, most preferably from 2.5% to 10%.

Suitable nonionic surfactants which may be used include in particular the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example aliphatic alcohols, acids, amides or alkyl phenols with alkylene oxides, especially ethylene oxide either alone or with propylene oxide. Specific nonionic detergent compounds are alkyl  $(C_6-C_{22})$  phenols - ethylene oxide condensates, the condensation products of aliphatic  $(C_8-C_{18})$  primary or secondary, linear or branched alcohols with ethylene oxide, and products made by condensation of ethylene oxide with the reaction products of propylene oxide and ethylenediamine. Other so-called nonionic detergent compounds include long-chain tertiary amine oxides, long-chain tertiary phosphine oxides and dialkyl sulphoxides.

It is also possible to include organic detergency builders in the composition, for example the alkali metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates, polyacetyl carboxylates and polyhydroxysulphonates. Specific examples include sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediamine-tetraacetic acid, nitrilotriacetic acid, oxydisuccinic

acid, melitic acid, benzene polycarboxylic acids and citric acid.

Apart from the ingredients already mentioned, a number of optional ingredients may also be present, such as lather boosters, e.g. alkanolamides, particularly the monoethanolamides derived from palmkernel fatty acids and coconut fatty acids, lather depressants, oxygen-releasing bleaching agents such as sodium perborate and sodium percarbonate, peracid bleach precursors, chlorine-releasing bleaching agents such as trichloroisocyanuric acid. However, for light duty applications, it is usually preferred to omit bleaches. Inorganic salts such as sodium sulphate, and, usually present in very minor amounts, fluorescent agents, perfumes, enzymes such as proteases and amylases, germicides and colourants may also be included.

A preferred process for preparing compositions according to the invention comprises admixing at least some of the ingredients except the pearlescer and heating the resultant composition, admixing the pearlescer in the molten state with the composition, followed by cooling. Any other ingredients not included in the first admixing stage can be incorporated at any convenient subsequent stage.

The present invention will now be illustrated by the following Examples.

5	EXAMPLE I					
	Composition	l	]	I		
	-			weight		
10	PAS	(1)	14.5	_		
	Sodium hydroxide		0.0			
	Oleic acid		0.9			
15	LAS	(2)	0.0			
	Pearlescer	1.00				
	Water 77.40					
	Polymer	(4)	0.5	52		
20	Antifoam	(5)	0.1	10		
	Nonionic (6) 5.50					
	Bactericide	/preservative	(7) 0.0	02		
	Pearlescent		yes	S		
25						
	EXAMPLES II	-IV				
	Composition	ı	II	III	IV	A
30	% by weight					
	PAS	(1)	14.50	14.50	14.50	14.50
	NI	(6)	5.5	5.5	5.5	_
35	Oleic acid		-	0.90	-	-
	LAS	(2)	-	-	0.004	-
40	Polymer	(4)	0.52	0.52	0.52	0.52
	Pearlescer	(3)	1.0	1.0	1.0	1.0
	Preservativ	e (7)	0.02	0.02	0.02	0.02
	Dye		0.00012	0.00012	0.00012	0.00012
45	Perfume		0.35	0.35	0.35	0.35
	NaOH		0.04	0.04	0.04	0.04
	Antifoam	(5)	0.20	0.20	0.20	0.20
	Water		balance	balance	balance	balance

55

50

рН

Pearlescent

7.30

yes

7.30

yes

7.30

yes

7.30

no

- (1)  $C_{12}-C_{13}$  branched-chain alkyl sulphate sodium salt ex EniChem (contains some additional NaOH, amount specified is PAS only)
- (2)  $C_{10}-C_{12}$  alkylbenzene sulphonic acid
- (3) Ethylene glycol monostearate, ex Hoechst
- (4) Natrosol ® 250HR, High MW hydroxymethyl cellulose thickener, ex Aqualon UK
- (5) SE36 ® silicone emulsion ex Wacker
- (6)  $C_{12}-C_{14}$  fatty alcohol with an average of 7 moles of ethylene oxide per molecule, ex ICI
- (7) Myacide BT ®, a bronopol-based preservative ex Boots

The above Examples clearly show that the compositions I-IV of the invention containing a crystallisation enhancer were all pearlescent, whereas composition A despite the pearlescer but without the invention was not pearlescent.

## **Claims**

5

10

15

- 1. A pearlescent liquid detergent composition comprising an organic pearlescer, at least 5% by weight of a primary alkyl sulphate anionic surfactant and less than 2.5% by weight of a pearlescer crystallisation enhancer selected from the group of acids, salts, alcohols and esters having a hydrophobic moiety with an average of at least 16 carbon atoms and nonionic surfactants.
- 30 2. A composition according to claim 1, wherein the hydrophobic moiety has at least 18 carbon atoms.
  - **3.** A composition according to claims 1 or claim 2, wherein the pearlescer crystallisation enhancer is an alkylbenzene sulphonate.
- 4. A composition according to claim 1 or claim 2, wherein the pearlescer crystallisation enhancer is a nonionic surfactant.
  - 5. A composition according to claim 1 or claim 2, wherein the pearlescer crystallisation enhancer is a soap.
  - **6.** A composition according to any of claims 1-5, comprising a mixture of ABS and soap as pearlescer crystallisation enhancers.
- **7.** A composition according to claims 1-6, wherein the amount of the pearlescer crystallisation enhancer is from 0.005% to 1.5% by weight.
  - **8.** A composition according to claims 1-7, wherein the pearlescer is ethylene glycol monostearate or ethylene glycol distearate.
- 50 **9.** A composition according to claims 1-8, wherein the amount of the pearlescer is from 0.1% to 5% by weight of the total composition.
  - **10.** A composition according to claim 1-9, wherein the amount of the primary alkyl sulphate is from 10% to 20% by weight.
  - 11. A composition according to claims 1-10, which composition is isotropic.
  - **12.** A composition according to claim 1-11, further comprising a thickener.

55

40

	13.	A composition according to claim 1-12, wherein the total amount of all detergent actives is from 10% to $30\%$ by weight of the total composition.
_	14.	A composition according to claims 1-13, comprising from 65% to 85% by weight of water.
5	15.	A composition according to claims 1-14, which composition is substantially free from inorganic builder.
	16.	A composition according to claims 1-15, comprising from 1% to 15% by weight of nonionic surfactant.
10		
15		
20		
25		
30		
35		
00		
40		
45		
50		
55		