

①② **EUROPEAN PATENT APPLICATION**

②① Application number: 89201025.7

⑤① Int. Cl. 4: **C11D 9/04 , C11D 9/26 ,**
C11D 10/04

②② Date of filing: **20.04.89**

③③ Priority: **06.05.88 GB 8810822**

④③ Date of publication of application:
06.12.89 Bulletin 89/49

⑧④ Designated Contracting States:
CH DE ES FR GB IT LI NL SE

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⑤④ **Liquid detergent compositions.**

- ⑤⑦ Environmentally preferred, isotropic, aqueous, liquid detergents, comprising:
- (i) at least 20 % by weight of a surfactant system, of which at least 5 % by weight of the total composition is soap;
 - (ii) at least 5 % by weight of propylene glycol;
 - (iii) less than 5 mmol per litre of calcium;
- said composition being substantially free of a di- or tri-alkanolamine capable of forming a complex with soap. Preferably the compositions also comprise a boron compound and glycerol to provide good enzyme stability.

EP 0 344 828 A2

LIQUID DETERGENT COMPOSITIONS

The present invention relates to an isotropic, aqueous soap-containing, liquid detergent composition.

Isotropic, liquid detergents are those which have no lamellar structure. In almost all cases, either they are unbuilt, i.e. contain no agent for mitigating calcium ion-induced water hardness, or contain only builder which is dissolved, for example a salt of a suitable, organic, carboxylic acid derivative, polymer carboxylic acid derivative, soap or mixtures of such materials. The present invention is concerned with those isotropic detergent liquids which contain more than 5% by weight of soap.

It is known to incorporate alkanolamines, specifically mono-, di- and trialkanolamines, in isotropic, liquid detergents, for example as described in UK patent specification GB 1 590 445. They have also been included in soap-containing, unstructured liquids which also include anionic surfactants, for example in UK patent specification GB 1 600 018. Such alkanolamines are known to have a plural role in the product. They can act as buffering agents, hydrotropes (ensuring the solubilization of ingredients, thus inhibiting the salting-out of components, and the occurrence of surfactant structures resulting in unwanted high viscosities) and enzyme stabilizers, including in the presence of boric acid and water-soluble borates.

In recent times there have been legislative trends to limit or ban those ingredients of detergent compositions which some sources believe could have a detrimental effect on the environment. Included in that category are some alkanolamines. Thus, there is a need to find a replacement for these alkanolamines which can fulfil all of the same functions, yet be usable at realistic, economic levels in the product. It is particularly a problem to find replacements which fulfil these criteria in compositions with high levels of soap and other surfactants.

It is disclosed in GB 2 126 242 (Colgate-Palmolive) to formulate liquid detergent compositions comprising anionic and nonionic synthetic detergent active materials in combination with soap, propylene glycol and relatively high levels of calcium; similar systems are disclosed in EP 151 678 (Procter and Gamble), these compositions are however sometimes not entirely stable, especially when the compositions are stored at lower temperatures.

It has now surprisingly been found that stable di- and tri-alkanolamine free isotropic detergent compositions comprising substantial amounts of soap and propylene glycol can be prepared, provided that the calcium content of the compositions is maintained below a specific critical level.

Therefore the present invention provides an isotropic, aqueous, liquid detergent composition comprising:

(i) at least 20 % by weight of a surfactant system, of which at least 5 % by weight of the total composition is soap;

(ii) at least 5 % by weight of propylene glycol;

(iii) less than 5 mmol per litre of calcium;

said composition being substantially free of a di- or tri-alkanolamine capable of forming a complex with soap. Preferably, the composition is also substantially free from other amine or amide sources.

The calcium level in the compositions according to the present invention is preferably less than 5 mmol per litre, more preferred less than 3 mmol per litre especially preferred less than 1 mmol per litre. Most preferably the compositions according to the present invention are substantially free of calcium in that no calcium is added to the composition and that the only calcium present originates from impurities in the materials used (i.e. calcium impurities in tap water). The calcium level is calculated on the basis of the total of calcium ions and calcium salts.

Compositions according to the invention are substantially free of di- or tri-alkanolamines, the level of these components will therefore generally be less than 0.5 % by weight of the composition, more preferred less than 0.1 %, especially preferred less than 0.02 %, most preferred compositions according to the invention are free of these di- or trialkanolamines.

Preferably, the composition contains at least 7.5% by weight of propylene glycol, most preferably at least 10%. A typical suitable amount is around 15% by weight. In most cases the propylene glycol will not exceed 20% by weight of the composition.

We have found that as well as being able to replace these alkanolamines, the aforementioned use of propylene glycol has the additional advantage that it assists removal of stains which are normally susceptible to bleach.

When enzymes are included, for instance at levels of from 0.1 to 2 % by weight of the composition, then the compositions of the present invention preferably also contain boric acid, boric oxide, borax or sodium ortho-, meta- or pyroborate, generally at from 0.25 to 15%, preferably from 0.5 to 10%, most preferably from 0.5 to 3% by weight of the composition, the amount being calculated as boric acid

containing an equivalent amount of boron.

The weight ratio of propylene glycol to the boron compound is preferably more than 5:1; especially suitable are ratios of between 5:1 and 20:1, preferably about 10:1.

When such a boron containing compound is present, it is preferred also to incorporate glycerol, although the amount required is generally somewhat less than that which would be required in the absence of the propylene glycol. Typical glycerol levels in the compositions of the present invention are from 1 to 10% by weight, more preferred from 1 to 5 %, typically around 2.5%.

Especially suitable is the use of a combination of propylene glycol, boron compound and glycerol in weight ratios of from 5 to 20 : 1 : 1 to 5, more preferred from 7 to 15 : 1 : 2 to 4. The enzyme stability in liquid compositions comprising this ternary combination of propylene glycol, glycerol and boron compounds has been found to be surprisingly good.

By the term 'soap' is meant an alkali metal soap of a long chain mono- or dicarboxylic acid, for example one containing 12 to 18 carbon atoms. Typical acids of this kind are oleic acid, ricinoleic acid and dodecyl succinic acid, fatty acids derived from castor oil, rapeseed oil, groundnut oil, coconut oil, palmkernel oil or mixtures thereof. The sodium or potassium soaps of these acids can be used, including mixtures of both forms.

Although the compositions according to the present invention contain more than 5% by weight of the soap, there is no upper limit for the soap content; so, for example, up to 50% by weight may be present. Typical amounts will be in the range of from 20 to 45% by weight, for example around 30%.

The compositions of the invention preferably contain, as well as the soap, one or more synthetic surfactants, preferably selected from the anionic, nonionic, cationic, zwitterionic and amphoteric classes.

Many suitable detergent-active compounds are commercially available and are fully described in the literature, for example in "Surface Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch.

The preferred synthetic surfactants which can be used are synthetic anionic compounds. These 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 are sodium and potassium primary or secondary alkyl sulphates, especially those obtained by sulphating the higher (C_8 - C_{18}) alcohols produced by reducing the glycerides of tallow or coconut oil; sodium and potassium alkyl (C_9 - C_{20}) benzene sulphonates, particularly sodium linear secondary alkyl (C_{10} - C_{15}) benzene sulphonates; 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 acid monoglyceride sulphates and sulphonates; sodium and potassium salts of sulphuric acid esters of higher (C_9 - C_{18}) fatty alcohol-alkylene oxide, particularly ethylene oxide, reaction products; the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid neutralized with sodium hydroxide; primary or secondary alkane monosulphonates such as those derived by reacting alpha-olefins (C_8 - C_{20}) with sodium bisulphite and those derived by reacting paraffins with SO_2 and Cl_2 and then hydrolyzing with a base to produce a random sulphonate; and olefin sulphonates, which term is used to describe the material made by reacting olefins, particularly alpha-olefins, with SO_3 and then neutralizing and hydrolyzing the reaction product.

Although, in general, the sodium salts of the anionic surfactants are preferred for cost reasons, the potassium salts can sometimes be used to advantage, particularly in compositions with high levels of other sodium salts such as sodium tripolyphosphate. Mixtures of potassium and sodium salts are also possible. It is, however, preferred that the composition should be substantially free of phosphates.

Of the anionic surfactant compounds, alkali metal alkyl (C_{10} - C_{15}) benzene sulphonates are particularly preferred, both for ready availability and cost and also for their advantageous solubility properties.

If desired, nonionic synthetic surfactants may be used as the sole detergent compounds, or, preferably, in admixture with anionic detergent compounds, especially the alkyl benzene sulphonates. Examples include the reaction products of alkylene oxides, usually ethylene oxide, with alkyl (C_6 - C_{22}) phenols, generally 5 to 25 EO, i.e. 5 to 25 units of ethylene oxide per molecule; the condensation products of aliphatic (C_8 - C_{18}) primary or secondary alcohols with ethylene oxide, generally 2 to 30 EO, e.g. 6 to 20 EO. Another example of suitable nonionics are nonionics obtained by first ethoxylating and subsequently propoxylating an organic hydroxyl group-containing radical, e.g. an aliphatic primary or secondary C_8 - C_{18} alcohol. Other so-called nonionic, detergent-active compounds include long chain tertiary phosphine oxides and dialkyl sulfoxides.

Mixtures of synthetic surfactants, for example mixed anionic or mixed anionic and nonionic compounds, may be used in detergent compositions, particularly to impart thereto controlled low sudsing properties or to improve the detergency. This is particularly beneficial for compositions intended for use in suds-intolerant

automatic washing machines.

Amounts of amphoteric or zwitterionic synthetic surfactants can also be used in the liquid detergent compositions of the invention, but this is not normally desired owing to their relatively high cost. If any amphoteric or zwitterionic synthetic surfactants are used, they will generally be incorporated in small amounts in compositions based on the much more commonly used anionic and/or nonionic surfactants.

The amount of synthetic surfactant material (if any) will generally be in the range of from about 2.0% to about 20%, preferably about 5% to about 15%, by weight of the composition, depending on the desired properties and, of course, provided that the amount of soap plus synthetic surfactants exceeds 20% by weight. Most preferred are mixed anionic/nonionic systems of synthetic surfactants, preferably with around 2-7.5% by weight of the anionic, typically about 5%, and around 5-15% by weight of the nonionic, typically around 10%.

The liquid detergent compositions of the invention can contain any of the conventional additives in the amounts in which such additives are normally employed in liquid fabric washing detergent compositions. Examples of these additives include lather depressants such as alkyl phosphates, silicones, anti-re-deposition agents such as sodium carboxymethyl cellulose, alkaline salts such as sodium silicate, alkali metal carbonates such as potassium carbonate or alkali metal hydroxides, fabric softening agents and, usually present in very minor amounts, fluorescent agents, perfumes, enzymes such as proteases and amylases, as well as germicides and colourants.

The compositions according to the present invention optionally also comprise a bleach, preferably a peroxide bleach. Examples of suitable peroxide compounds include hydrogen peroxide, the alkali metal peroxides, the perborates, persulfates, peroxy disulfates, perphosphates, the crystalline peroxyhydrates formed by reacting hydrogen peroxide with urea i.e. urea peroxide or with alkali metal carbonate i.e. alkalimetal percarbonates. Also encapsulated bleaches may be used. Preferred peroxide bleaches are sodium perborate tetra- and mono hydrates and sodium percarbonate. Preferably the bleaches are only partially soluble in the system. The bleach component is preferably added in an amount corresponding to 0.1 to 15% by weight of active oxygen, more preferred from 0.5 to 10% active oxygen, typically from 1.0 to 5.0% active oxygen. If the bleach is hydrogen peroxide, this is preferably used at a level of from 1.5 to 7.5 % by weight of the composition, preferably in such an amount that it can deliver from about 100 to 150 mg/litre active oxygen in the wash.

The bleach component may be present in the system in solubilized form, but also possible is that only part of the peroxygen bleach is solubilized, the remaining part being present as solid particles which are suspended in the system.

Such solid particles may be added as such to the composition, preferably however, they are formed by in situ crystallisation. For perborate bleach particles this preferably involves the in situ crystallization of a perborate tetrahydrate such as for instance disclosed in EP 294 904 (Procter and Gamble). Other methods for effecting the presence of bleach in solid form are described in EP 293 040 (Procter and Gamble); these involve the addition of one or more water-miscible solvents.

The balance of the composition is water, which is usually present to the extent of about 40% to about 75% by weight, preferably about 45% to about 65% by weight.

To ensure effective detergency, the liquid detergent compositions should be alkaline, and it is preferred that they should provide a pH within the range of about 8.5 to 12, preferably about 9 to about 11, when used in aqueous solutions of the composition at the recommended concentration. To meet this requirement, the undiluted liquid composition should preferably be of a pH between 7 and 12.5, for example about pH 8.5 to about 12.5. It should be noted that an excessively high pH, e.g. over about pH 13, is less desirable for domestic safety. If a bleach such as hydrogen peroxide is present in the liquid composition, then the pH is generally from 7.5 to 10.5, preferably 8 to 10, and especially 8.5 to 10, to ensure the combined effect of good detergency and good physical and chemical stability. The ingredients in any such highly alkaline detergent composition should, of course, be chosen for alkaline stability, especially for pH-sensitive materials such as enzymes, and a particularly suitable proteolytic enzyme. The pH may be adjusted by addition of a suitable alkaline material.

The viscosity of the liquid detergent should preferably be less than 1000 mPas at 25 °C, measured at 21 S⁻¹, more preferably less than 500 mPas; especially suitable are viscosities of 80 to 400 mPas.

As well as the propylene glycol, it is possible for the composition to contain an additional (alkaline) buffer, for example an alkali metal carbonate such as potassium carbonate, to maintain the pH of at least 8.5 during use, particularly, for example, in hard water or at low product concentrations.

The compositions of the invention may be prepared in any suitable way; a preferred method is, however, dissolving the alkali (for the in situ neutralization of anionic surfactant and fatty acids) in water of room temperature, adding any acidic anionic surfactant and the propylene glycol, and heating the mix to

55 °C under agitation. Subsequently, a pre-mix consisting of any nonionic active, fatty acid and, if required, the lather booster with a temperature above the melting temperature of the components, should be dissolved in the mix. The builder and buffer salts should preferably be added as the final components, as well as the bleach e.g. hydrogen peroxide, if present.

5 In use the liquid detergent compositions of the present invention will generally be diluted with water to form an aqueous wash liquor for the washing of fabrics, for example in a washing machine. Preferably the wash liquor will comprise from 0.1 to 10 % by weight of the liquid detergent composition, preferably from 5 to 15 g/litre.

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

10 Example I

INGREDIENT	% by weight
Dodecyl benzene sulphonic acid Na salt	4.8
C ₁₃ -C ₁₅ (7 EO) alcohol nonionic	9.6
Topped coconut fatty acid	12.3
Oleic acid	17.8
KOH	3.5
NaOH	2.5
Glycerol	2.5
Propylene glycol	14.0
Ethanol	3.5
Boric acid	1.0
Enzyme	0.5
Minor components	0.9
Water	balance

The composition was prepared by dissolving KOH and NaOH in water of room temperature, adding the dodecyl benzene sulphonic acid Na salt, boric acid and diol and heating the mix under agitation. Subsequently, a pre-mix of C₁₃-C₁₅ (7 EO) alcohol nonionic, coconut fatty acid and oleic acid with a temperature above the melting temperature of the ingredients was dissolved in the mix. The remaining components were finally added.

The final product had a viscosity of 240 mPas at 25 °C as measured at 21 s⁻¹, and a pH of 9.4.

The product was used at a concentration of 10 g/l in a Miele W 765 at 40 °C. Compared with a triethanolamine- containing, liquid detergent (Sunil), it showed better bleachable stain removal of, for instance, tea, blackberries and red wine.

Example II

45 Enzyme stability at 37 °C was measured for compositions as described in Example I wherein the glycerol level was varied. Table I shows the stability of the enzyme Savinase 16.0 L grade at 37 °C after 9 weeks (pH = 9.6).

% glycerol	% enzyme activity * after 8/9 weeks
0	38
2	44
2.5	48
3	61

* results expressed in % residual activity

Examples III-VIII

The following compositions were prepared by dissolving the NaOH and KOH in water of room temperature, adding the anionic surfactant, boric acid and propylene glycol and heating the mix under agitation. Subsequently, a pre-mix of the ethoxylated materials and the fatty acid having a temperature above the melting temperature of the ingredients was dissolved in the mix. The remaining components were finally added.

	Ex III	Ex IV	Ex V
Dodecyl benzene sulphonic acid, Na salt	5.0	-	-
Secondary alkyl sulphonic acid, Na-salt	-	5.0	-
C ₁₃ -C ₁₅ (7 EO) alcohol nonionic	10.0	-	-
Coconut (10 EO) alcohol nonionic	-	10.0	10.0
Topped coconut fatty acid	11.0	11.0	11.0
Oleic acid	16.0	16.0	16.0
NaOH	1.6	2.4	2.4
KOH	4.4	3.4	3.4
Glycerol	3.5	2.5	-
Propylene glycol	12.0	15.0	15.0
Ethanol	3.5	2.5	2.5
Boric acid	1.0	1.0	1.0
Enzyme	0.5	0.5	0.5
Minor components	0.9	-	-
Water	-----balance-----		
	Ex 6	Ex 7	Ex 8
Dodecyl benzene sulphonic acid, Na salt	2.5	4.8	8.9
C ₁₃ -C ₁₅ (7 EO) alcohol nonionic	7.0	9.6	12.0
Topped coconut fatty acid	8.1	11.0	14.1
Oleic acid	16.7	16.0	3.4
NaOH	2.2	1.4	-
KOH	3.0	4.2	5.6
Glycerol	3.5	3.0	3.5
Propylene glycol	8.0	12.0	9.0
Ethanol	4.5	3.5	2.5
Boric acid	1.0	1.0	1.5
Na carbonate	-	1.5	2.5
Enzyme	0.5	0.5	0.6
Minor components	0.9	0.9	0.9
Water	-----balance-----		

The following compositions were made as examples 3 to 8.

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	Ex 9	Ex 10
INGREDIENT	weight %	
H ₂ O	-----balance-----	
KOH	2.57	2.57
NaOH	1.91	1.91
Boric acid	1.00	1.00
Fluorescer (Tinopal CBS-X)	0.06	0.06
Propylene Glycol	8.00	8.00
Glycerol	3.34	3.34
C12-14 Alkyl benzene sulphonate	7.69	7.69
ethoxylated C13-15 alcohol 7EO	19.00	19.00
Polydimethylsiloxane	0.03	0.03
Fatty acid mixture(60/40 oleic/topped coconut)	15.00	15.00
Protease (Savinase 16.0 L)	0.26	0.34
Perfume	0.35	0.35
Opacifier	3.00	3.00
Dye solution	0.10	0.10
Amylase	-	0,10
Dequest 2066	-	2,77

The following composition was made as in examples 3 to 8.

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Example	Ex 11
INGREDIENT	weight %
H ₂ O	balance
sodium citrate	1.20
sodium formate	0.90
NaOH	1.89
Fluorescer	0.13
Propylene Glycol	10.00
Glycerol	3.50
C12-14 ABS (MARLON AS3)	11.50
PAS	3.00
ethoxylated C13-15 alcohol 7EO	13.00
Dodecenyl succinic acid	10.62
Fatty acid (Priolene 6902)	3.54
Protease (Savinase 16.0 L)	0.65
Amylase	0.25
Aminosilane	0.05
Opacifier	0.30
Dye solution (1%)	0.10
Dequest 2066	0.87

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Claims

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1. An isotropic, aqueous, liquid detergent composition comprising:
 - (i) at least 20 % by weight of a surfactant system, of which at least 5 % by weight of the total composition is soap;
 - (ii) at least 5 % by weight of propylene glycol;
 - (iii) less than 5 mmol per litre of calcium;
 said composition being substantially free of a di- or tri-alkanolamine capable of forming a complex with soap.

2. A composition according to Claim 1, further comprising an enzyme and boric acid or a salt thereof, capable of stabilizing an enzyme in the composition, in the presence of propylene glycol.

3. A composition according to Claim 1 or 2, also comprising from 1 to 5 % by weight of glycerol.

4. A composition according to Claim 1 and 2 and 3, wherein the weight ratio of propylene glycol to
5 boron compound to glycerol is from 5 to 20 : 1 : 1 to 5.

5. A composition according to Claim 1, 2, 3 or 4, having a viscosity of less than 1000 mPas at 25 °C, measured at 21 S⁻¹.

6. A composition according to one or more of the claims 1-5, having a pH of from 7 to 12.5.

7. A composition according to one or more of Claims 1-6, comprising 2.0 to 20% by weight of a
10 synthetic surfactant material.

8. Method for treating fabrics comprising contacting the fabrics with an aqueous liquor comprising a detergent composition according to Claim 1.

9. Method according to Claim 8, characterized in that the aqueous liquor comprises 5-15 g/l of the detergent composition.

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