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(54) Title: DETERGENT COMPOSITION

(57) Abstract: The invention provides a cleaning composition comprising: (i) from 0.1 to 40 wt.% of a saponin; and, (ii) from 0.1 to 20 wt.% of an alkyl ether carboxylic acid surfactant of the following structure: $R_2-(OCH_2CH_2)_n-OCH_2-COOH$, wherein: R_2 is selected from saturated and mono-unsaturated C_{10} to C_{20} linear or branched alkyl chains, wherein n is selected from 5 to 30, and wherein the weight fraction of alkyl ether carboxylic acid to saponin is from 0.05 to 10, preferably from 0.1 to 3; the invention further relates to a domestic method of treating a textile and to the use of a combination of saponin and alkyl ether carboxylic acid surfactant in a detergent composition to provide reduced foam levels compared to expected foam levels in a detergent composition, wherein the weight fraction of alkyl ether carboxylic acid to saponin is from 0.05 to 10, preferably from 0.1 to 3.



DETERGENT COMPOSITION

Field of Invention

- 5 The invention concerns a cleaning composition comprising a saponin and an alkyl ether carboxylic acid surfactant.

Background of the Invention

- 10 Alternative surfactants can provide versatility to the formulator to provide better cleaning composition.

Some surfactants when used as detergent actives in cleaning compositions, in particular laundry cleaning compositions, produce large quantities of foam which is difficult to remove without using excess water.

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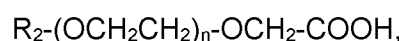
Using alkyl ether carboxylic acid surfactants for example, it would be desirable to reduce the foam produced. This problem is particularly pronounced in laundry detergent formulations, especially liquid laundry detergent formulations.

Summary of the Invention

- 20 We have found that the incorporation of saponins in cleaning compositions comprising alkyl ether carboxylic acid surfactants reduces the foam produced. This is unexpected as saponins themselves are expected to produce quite a lot of foam.

- 25 In one aspect the present invention provides a cleaning composition comprising:

- (i) from 0.1 to 40 wt.%, preferably from 0.25 to 30 wt.%, more preferably from 0.5 to 25 wt.%, more preferably from 0.5 to 20 wt.%, most preferably from 0.5 to 15 wt.%, of a saponin; and,
- (ii) from 0.1 to 20 wt.% of an alkyl ether carboxylic acid surfactant of the following
- 30 structure:



wherein:

R₂ is selected from saturated and mono-unsaturated C₁₀ to C₂₀ linear or branched alkyl chains, preferably selected from: C₁₂; C₁₄; C₁₆; and, C₁₈ linear alkyl chains, wherein n is selected from 5 to 30, preferably from 6 to 20, more preferably from 8 to 16, and wherein the weight fraction of alkyl ether carboxylic acid to saponin is from 0.05 to 10, preferably from 0.1 to 3.

Preferably the composition comprises from 0.5 to 6 wt.%, more preferably from 1 to 6 wt.%, most preferably from 2 to 6 wt.% of the alkyl ether carboxylic acid anionic surfactant.

Preferably the alkyl chain, the R₂ group, of the alkyl ether carboxylic acid anionic surfactant is selected from saturated and mono-unsaturated C₁₆ to C₁₈ linear alkyl chains.

Preferably the saponin has a triterpenoid backbone, and one or more sugar moieties attached to the triterpenoid backbone. More preferably there are at least two sugar moieties attached to the triterpenoid backbone.

Preferably the composition comprises from 1 to 60 wt.%, preferably from 2.5 to 50 wt.%, more preferably from 4 to 40 wt.%, most preferably from 8 to 35 wt.% of a surfactant, said surfactant not including saponin.

Preferably the composition comprises anionic and/or nonionic surfactant, more preferably the composition comprises both anionic and nonionic surfactant.

A preferred detergent composition is a laundry detergent composition, preferably the laundry detergent composition is a liquid, gel or a powder, more preferably the laundry detergent is a liquid detergent, most preferably an aqueous laundry detergent composition.

The laundry detergent preferably comprises an alkoxyated polyamine. Preferred levels of alkoxyated polyamine are from 0.1 to 8 wt.%, more preferably from 0.2 to 6 wt.%, most preferably from 0.5 to 5 wt.%. Preferably the alkoxyated polyamine is an alkoxyated polyethylenimine, and/or alkoxyated polypropylenimine, more preferably the alkoxylation is ethoxylation or propoxylation or a mixture of both.

The laundry detergent composition preferably comprises a soil release polymer, preferably at a level of from 0.1 to 8 wt.%, more preferably from 0.2 to 6 wt.%, most preferably from 0.5 to 5 wt.%, preferably the soil release polymer is a polyester soil release polymer.

- 5 Preferred detergent compositions, particularly laundry detergent compositions additionally comprise one or more enzymes selected from lipases, proteases, amylases, cellulases, and mixtures thereof.

10 Preferably, wherein when a liquid laundry detergent, the laundry detergent composition when dissolved in demineralised water at 4g/L, 293K has a pH of from 6 to 11, more preferably from 7 to 9.

In another aspect the present invention provides a domestic method of treating a textile, the method comprising the steps of:

- 15 a) treating a textile with from 1 g/L of an aqueous solution of the cleaning composition as defined the first aspect of the invention; and,
b) allowing said aqueous solution to remain in contact with the textile for a time period of from 10 minutes to 2 days, then rinsing and drying the textile.

20 In another aspect, the invention provides the use of a combination of saponin and alkyl ether carboxylic acid surfactant in a detergent composition to provide reduced foam levels compared to expected foam levels in a detergent composition, wherein the weight fraction of alkyl ether carboxylic acid to saponin is from 0.05 to 10, preferably from 0.1 to 3.

25 **Detailed Description of the Invention**

The indefinite article “a” or “an” and its corresponding definite article “the” as used herein means at least one, or one or more, unless specified otherwise.

30 All % levels of ingredients in compositions (formulations) listed herein are in wt.% based on total formulation unless other stated.

It is understood that any reference to a preferred ingredient of the cleaning composition is envisaged to be combinable subject matter with any other preferred ingredient of the
35 cleaning composition disclosed herein.

The cleaning composition may take any suitable form, for example liquids, solids (including powders) or gels.

- 5 The cleaning composition can be applied to any suitable substrate, including but not limited to any substrate to which a home care composition would be applied, for example, textiles, crockery and cutlery. Particularly preferred substrates are textiles. Particularly preferred detergent compositions are laundry detergent compositions. Preferably the laundry detergent composition is a liquid, gel or a powder, more preferably the detergent is a liquid
10 detergent.

Laundry detergent compositions may take any suitable form. Preferred forms are liquid or powder, with liquid being most preferred.

15 **Alkyl Ether Carboxylic Acid**

The cleaning composition comprises from 0.1 to 20 wt.%, preferably from 0.5 to 6 wt.%, more preferably from 1 to 6 wt.%, most preferably from 2 to 6 wt.% of the alkyl ether carboxylic acid anionic surfactant.

- 20 Weights of alkyl ether carboxylic acid are calculated as the protonated form, $R_2-(OCH_2CH_2)_n-OCH_2COOH$. The alkyl ether anionic surfactant may be in carboxylic acid form, or it may be in alkyl ether carboxylate surfactant form. The alkyl ether carboxylate/carboxylic acid anionic surfactant may be used as salt version, for example with a counterion such as a sodium salt, or an amine salt.

25

The alkyl chain may be linear or branched, preferably it is linear.

The alkyl chain may be aliphatic or contain one cis or trans double bond.

- 30 The alkyl chain (R_2) is selected from saturated and mono-unsaturated C_{10} to C_{20} linear or branched alkyl chains preferably selected from: C_{12} ; C_{14} ; C_{16} ; and, C_{18} linear alkyl chain. The alkyl chain is preferably selected from $CH_3(CH_2)_{11}$, $CH_3(CH_2)_{13}$, $CH_3(CH_2)_{15}$, $CH_3(CH_2)_{17}$, $CH_3(CH_2)_7CH=CH(CH_2)_8$ -. It is preferred that the R_2 is selected from C_{16} to C_{18} linear alkyl chains. Most preferably the alkyl chain is $CH_3(CH_2)_7CH=CH(CH_2)_8$ -.
35

The alkyl ether carboxylic acid has n selected from 5 to 30, preferably from 6 to 20, more preferably from 8 to 16.

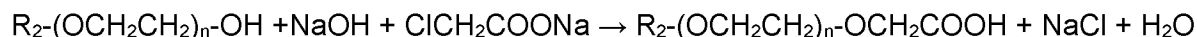
5 The weight fraction of alkyl ether carboxylic acid to saponin is from 0.05 to 10, preferably from 0.1 to 3.

Alkyl ether carboxylic acid are available from Kao (Akypo®), Huntsman (Empicol®) and Clariant (Emulsogen®).

10 Alkyl ether carboxylic acids synthesis is discussed in Anionic Surfactants Organic Chemistry edited by H.W. Stache (Marcel Dekker, New York 1996).

They may be synthesised via the reaction of the corresponding alcohol ethoxylate with chloroacetic acid or monochloro sodium acetate in the presence of NaOH:-

15

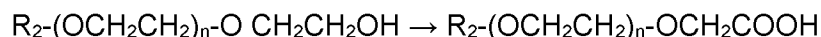


In this synthesis residual $R_2-(OCH_2CH_2)_n-OH$ may be present, preferably levels of $R_2-(OCH_2CH_2)_n-OH$ are from 0 to 10 wt.% in the alkyl ether carboxylic acid. Low levels of diglycolic acid and glycolic acid may be present as bi products.

20

NaCl from the synthesis may be present in the aqueous liquid laundry detergent composition. Additional NaCl may be added to the composition.

25 They alkyl ether carboxylic acid may also be synthesised via an oxidation reaction:-



The oxidation is typically conducted using oxygen as the oxidant under basic conditions in the presence of metal catalyst such as Pd/Pt, as described in DE3135946; DE2816127 and EP0304763.

30

Saponin

The composition comprises from 0.1 to 40 wt.%, preferably from 0.25 to 30 wt.%, more preferably from 0.5 to 25 wt.%, more preferably from 0.5 to 20 wt.%, most preferably from 0.5 to 15 wt.%, of a saponin.

5

Saponins are natural compounds which contain sugar moieties bound to a fused system of non-aromatic 4, 5 and 6 membered rings. The ring system are preferably selected from the groups of triterpenoids, for example lanostane, dammarane, lupane, oleanane, ursane and hopane. An overview of these ring systems is provided in Natural Product Reports

10 (2010), 79-132 by R.A. Hill *et al.*

Saponins are discussed in "Saponins Used in Food and Agriculture" Plenum Press, New York 1996, G. R. Waller and K. Yamasaki (eds).

15 Saponins are preferably extracted from the seed, root, leaf, bulb, fruit, stem, pericarp, bark, tuber or flower of a plant. Saponin extraction and quantification is discussed in Food Research International **59** (2014) 16-40 by R. Sulaiman *et al.* Extraction of saponins from agricultural products is discussed in WO2017/019599 and WO1999/053933.20 Saponins may also be produced by bacteria (for example glycosylated hopanoids such as ribosylhopane) and marine organisms including sea cucumbers, starfish and sponges (Bahrami, Y., Zhang, W. & Franco, C.M. (2018) Marine Drugs 16: 423-453). Saponins may also be produced through biotechnology, either through enzymatic biosynthesis in vitro or by the engineering of microbial cell factories (Moses, T. *et al.* (2014) PNAS 28:1634-1639).

25

The saponin is preferably a Tea saponin (for example preferably derived from *Camellia* species), Soapnut saponin (for example preferably derived from *Sapindus* species), Quillaja Bark saponin or Escin (for example preferably derived from *Aesculus* species).

30 Preferably the saponin has a structure comprising a triterpenoid backbone and one or more sugar moieties attached to the triterpenoid backbone.

Saponins are listed in the Chemical Entities of Biological Interest (ChEBI) database, (Hastings, J., de Matos, P., Dekker, A., Ennis, M., Harsha, B., Kale, N., Muthukrishnan, V.,

35 Owen, G., Turner, S., Williams, M., and Steinbeck, C. (2013) The ChEBI reference database

and ontology for biologically relevant chemistry: enhancements for 2013. *Nucleic Acids Res.*). For example, CHEBI:61778 - triterpenoid saponin.

Agricultural residues remaining after harvest may be suitable for extraction and supply of saponins. For example, sugarbeet leaves and skins may be further extracted to derive useful quantities of saponin. In China, the production and supply of tea saponin derived from the seed cake remaining after extraction of *Camellia oleifera* seeds for tea seed oil is well established. Alternatively, saponins may be extracted from parts of the plant collected from the wild (for example, protodioscin from *Tribulus terrestris*) or through managed plantations (for example from the bark of *Quillaja saponaria*).

Preferred Ingredients

Surfactant

The cleaning composition preferably comprises surfactant (which includes a mixture of two or more surfactants). The composition comprises from 1 to 60 wt.%, preferably from 2.5 to 50 wt.%, more preferably from 4 to 40 wt.% of surfactant. Even more preferred levels of surfactant are from 6 to 40 wt.%, more preferably from 8 to 35 wt.%.

Suitable anionic detergent compounds which may be used 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 alkyl radicals.

Examples of suitable synthetic anionic detergent compounds are rhamnolipids, sodium and potassium alkyl sulphates, especially those obtained by sulphating higher C₈ to C₁₈ alcohols, produced for example from tallow or coconut oil, sodium and potassium alkyl C₉ to C₂₀ benzene sulphonates, particularly sodium linear secondary alkyl C₁₀ to C₁₅ benzene sulphonates; and sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum.

The anionic surfactant is preferably selected from: rhamnolipids, linear alkyl benzene sulphonate; alkyl sulphates; alkyl ether sulphates; soaps; alkyl (preferably methyl) ester sulphonates, and mixtures thereof.

The most preferred anionic surfactants are selected from: rhamnolipids, linear alkyl benzene sulphonate; alkyl sulphates; alkyl ether sulphates and mixtures thereof. Preferably the alkyl ether sulphate is a C₁₂-C₁₄ n-alkyl ether sulphate with an average of 1 to 3EO (ethoxylate) units.

5

Sodium lauryl ether sulphate is particularly preferred (SLES). Preferably the linear alkyl benzene sulphonate is a sodium C₁₁ to C₁₅ alkyl benzene sulphonates. Preferably the alkyl sulphates is a linear or branched sodium C₁₂ to C₁₈ alkyl sulphates. Sodium dodecyl sulphate is particularly preferred, (SDS, also known as primary alkyl sulphate).

10 Rhamnolipids may preferably be mono-rhamnolipid rich (over 60%), di-rhamnolipid rich (over 60%), or a 40/60 to 60-40 mixture of mono- and di-rhamnolipid.

In liquid formulations preferably two or more anionic surfactant are present, for example linear alkyl benzene sulphonate together with an alkyl ether sulphate.

15

In liquid formulations, preferably the laundry composition in addition to the anionic surfactant comprises alkyl ethoxylated non-ionic surfactant, preferably from 2 to 8 wt.% of alkyl ethoxylated non-ionic surfactant.

20 Suitable nonionic detergent compounds which may be used include, in particular, the reaction products of compounds having an aliphatic hydrophobic group and a reactive hydrogen atom, for example, aliphatic alcohols, acids or amides, especially ethylene oxide either alone or with propylene oxide. Preferred nonionic detergent compounds are the condensation products of aliphatic C₈ to C₁₈ primary or secondary linear or branched
25 alcohols with ethylene oxide. Alkyl polyglycosides (APG) are also preferred.

Most preferably the nonionic detergent compound is the alkyl ethoxylated non-ionic surfactant is a C₈ to C₁₈ primary alcohol with an average ethoxylation of 7EO to 9EO units.

30 Preferably the surfactants used are saturated.

Soil release polymer

It is preferred that a soil release polymer is included.

The laundry detergent composition preferably comprises from 0.1 to 8 wt.% of a polyester soil release polymer.

Preferred levels of soil release polymer range from 0.2 to 6 wt.%, more preferably from 0.25 to 6 wt.%, even more preferably from 0.5 to 5 wt.%, most preferably from 1 to 5 wt.%.

More preferably the polyester soil release polymer is a polyethylene and/or polypropylene terephthalate based soil release polymer, most preferably a polypropylene terephthalate based soil release polymer.

Suitable polyester based soil release polymers are described in WO 2014/029479 and WO 2016/005338.

Alkoxylated polyamine

When the detergent composition is in the form of a laundry composition, it is preferred that an alkoxylated polyamine is included.

The laundry detergent preferably comprises from 0.1 to 8 wt.% of an alkoxylated polyamine.

Preferred levels of alkoxylated polyamine range from 0.2 to 6 wt.%, more preferably from 0.5 to 5 wt.%. Another preferred level is from 1 to 4 wt.%.

The alkoxylated polyamine may be linear or branched. It may be branched to the extent that it is a dendrimer. The alkoxylation may typically be ethoxylation or propoxylation, or a mixture of both. Preferably the alkoxylated polyamine comprises an alkoxylated polyethylenimine, and/or alkoxylated polypropylenimine, more preferably the alkoxylation is ethoxylation or propoxylation or a mixture of both. Where a nitrogen atom is alkoxylated, a preferred average degree of alkoxylation is from 10 to 30, preferably from 15 to 25.

A preferred material is alkoxylated polyethylenimine, most preferably ethoxylated polyethyleneimine, with an average degree of ethoxylation being from 10 to 30 preferably from 15 to 25, where a nitrogen atom is ethoxylated.

Enzymes

Enzymes, may be present in the cleaning composition. It is preferred that enzymes are present in the preferred laundry detergent composition.

- 5 If present, then the level of each enzyme in the composition of the invention is from 0.0001 wt.% to 0.1 wt.%.

Levels of enzyme present in the composition preferably relate to the level of enzyme as pure protein.

10

Preferred enzymes include those in the group consisting of: proteases, lipases, cellulases, alpha-amylases, peroxidases/oxidases, pectate lyases, and/or mannanases. Said preferred enzymes include a mixture of two or more of these enzymes.

- 15 Preferably the enzyme is selected from: proteases, lipases, cellulases, and/or alpha-amylases.

Preferred proteases are selected from the following group, serine, acidic, metallo- and cysteine proteases. More preferably the protease is a serine and/or acidic protease.

20

Preferably the protease is a serine protease. More preferably the serine protease is subtilisin type serine protease.

- 25 Protease enzymes hydrolyse bonds within peptides and proteins, in the cleaning context this leads to enhanced removal of protein or peptide containing stains. Serine proteases are preferred. Subtilase type serine proteases are more preferred. The term "subtilases" refers to a sub-group of serine protease according to Siezen et al., Protein Engng. 4 (1991) 719-737 and Siezen et al. Protein Science 6 (1997) 501 -523. Serine proteases are a subgroup of proteases characterized by having a serine in the active site, which forms a covalent
- 30 adduct with the substrate. The subtilases may be divided into 6 sub-divisions, i.e. the Subtilisin family, the Thermitase family, the Proteinase K family, the Lantibiotic peptidase family, the Kexin family and the Pyrolysin family.

- 35 Examples of subtilases are those derived from Bacillus species such as Bacillus lentus, B. licheniformis, B. alkalophilus, B. subtilis, B. amyloliquefaciens, B. pumilus and B. gibsonii,

and subtilisin lentus, subtilisin Novo, subtilisin Carlsberg, subtilisin BPN', subtilisin 309, subtilisin 147 and subtilisin 168, and protease PD138. Examples of trypsin-like proteases are trypsin (e.g. of porcine or bovine origin) and the *Fusarium* protease, and the chymotrypsin proteases derived from *Cellulomonas*.

5

Most preferably the protease is a subtilisin protease (EC 3.4.21.62).

Examples of subtilases are those derived from *Bacillus* such as *Bacillus lentus*, *B. alkalophilus*, *B. subtilis*, *B. amyloliquefaciens*, *Bacillus pumilus* and *Bacillus gibsonii*, and subtilisin lentus, subtilisin Novo, subtilisin Carlsberg, *Bacillus licheniformis*, subtilisin BPN', subtilisin 309, subtilisin 147 and subtilisin 168 and protease PD138. Preferably the subtilisin is derived from *Bacillus*, preferably *Bacillus lentus*, *B. alkalophilus*, *B. subtilis*, *B. amyloliquefaciens*, *Bacillus pumilus* and *Bacillus gibsonii*. Most preferably the subtilisin is derived from *Bacillus gibsonii* or *Bacillus Lentus*.

15

Suitable commercially available protease enzymes include those sold under the trade names names Carnival®, Relase®, Relase® Ultra, Savinase®, Savinase® Ultra, Coronase®, Coronase® Ultra, Kannase®, Liqueanase®, Liqueanase® Ultra, all could be sold as Ultra® or Eevity® (Novozymes A/S).

20

Suitable lipases include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Examples of useful lipases include lipases from *Humicola* (synonym *Thermomyces*), e.g. from *H. lanuginosa* (*T. lanuginosus*) or from *H. insolens*, a *Pseudomonas* lipase, e.g. from *P. alcaligenes* or *P. pseudoalcaligenes*, *P. cepacia*, *P. stutzeri*, *P. fluorescens*, *Pseudomonas* sp. strain SD 705, *P. wisconsinensis*, a *Bacillus* lipase, e.g. from *B. subtilis* (Dartois et al. (1993), Biochemica et Biophysica Acta, 1131, 253-360), *B. stearothermophilus* or *B. pumilus*.

25

Preferred commercially available lipase enzymes include Lipolase™ and Lipolase Ultra™, Lipex™ and Lipoclean™ (Novozymes A/S).

30

The invention may be carried out in the presence of phospholipase classified as EC 3.1.1.4 and/or EC 3.1.1.32. As used herein, the term phospholipase is an enzyme which has activity towards phospholipids.

35

Phospholipids, such as lecithin or phosphatidylcholine, consist of glycerol esterified with two fatty acids in an outer (sn-1) and the middle (sn-2) positions and esterified with phosphoric acid in the third position; the phosphoric acid, in turn, may be esterified to an amino-alcohol. Phospholipases are enzymes which participate in the hydrolysis of phospholipids. Several
5 types of phospholipase activity can be distinguished, including phospholipases A₁ and A₂ which hydrolyze one fatty acyl group (in the sn-1 and sn-2 position, respectively) to form lysophospholipid; and lysophospholipase (or phospholipase B) which can hydrolyze the remaining fatty acyl group in lysophospholipid. Phospholipase C and phospholipase D (phosphodiesterases) release diacyl glycerol or phosphatidic acid respectively.

10 The composition may use cutinase, classified in EC 3.1.1.74. The cutinase used according to the invention may be of any origin. Preferably cutinases are of microbial origin, in particular of bacterial, of fungal or of yeast origin.

15 Suitable amylases (alpha and/or beta) include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Amylases include, for example, alpha-amylases obtained from *Bacillus*, e.g. a special strain of *B. licheniformis*, or the *Bacillus* sp. strains disclosed in WO 95/026397 or WO 00/060060. Commercially available amylases are Duramyl™, Termamyl™, Termamyl Ultra™, Natalase™, Stainzyme™, Amplify™,
20 Fungamyl™ and BAN™ (Novozymes A/S), Rapidase™ and Purastar™ (from Genencor International Inc.).

Suitable cellulases include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Suitable cellulases include cellulases from the genera
25 *Bacillus*, *Pseudomonas*, *Humicola*, *Fusarium*, *Thielavia*, *Acremonium*, e.g. the fungal cellulases produced from *Humicola insolens*, *Thielavia terrestris*, *Myceliophthora thermophila*, and *Fusarium oxysporum*. Commercially available cellulases include Celluzyme™, Carezyme™, Celluclean™, Endolase™, Renozyme™ (Novozymes A/S), Clazinase™ and Puradax HA™ (Genencor International Inc.), and KAC-500(B)™ (Kao
30 Corporation). Celluclean™ is preferred.

Suitable peroxidases/oxidases include those of plant, bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Examples of useful peroxidases include peroxidases from *Coprinus*, e.g. from *C. cinereus*, and variants thereof.

Commercially available peroxidases include Guardzyme™ and Novozym™ 51004 (Novozymes A/S).

Enzyme Stabilizers

Any enzyme present in the composition may be stabilized using conventional stabilizing agents, e.g., a polyol such as propylene glycol or glycerol, a sugar or sugar alcohol, lactic acid, boric acid, or a boric acid derivative, e.g., an aromatic borate ester, or a phenyl boronic acid derivative such as 4-formylphenyl boronic acid, and the composition may be formulated as described in e.g. WO 92/19709 and WO 92/19708.

Further materials

Further optional but preferred materials that may be included in the cleaning compositions (preferably laundry detergent compositions) include builders, chelating agents, fluorescent agent, perfume, shading dyes and polymers.

Builders or Complexing Agents

The composition may comprise a builder.

Builder materials may be selected from 1) calcium sequestrant materials, 2) precipitating materials, 3) calcium ion-exchange materials and 4) mixtures thereof.

Examples of calcium sequestrant builder materials include alkali metal polyphosphates, such as sodium tripolyphosphate and organic sequestrants, such as ethylene diamine tetra-acetic acid.

Examples of precipitating builder materials include sodium orthophosphate and sodium carbonate.

Examples of calcium ion-exchange builder materials include the various types of water-insoluble crystalline or amorphous aluminosilicates, of which zeolites are well known representatives thereof, e.g. zeolite A, zeolite B (also known as zeolite P), zeolite C, zeolite X, zeolite Y and also the zeolite P-type as described in EP-A-0,384,070.

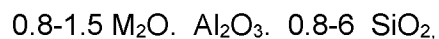
The composition may also contain 0-65 wt.% of a builder or complexing agent such as ethylenediaminetetraacetic acid, diethylenetriamine-pentaacetic acid, alkyl- or

alkenylsuccinic acid, nitrilotriacetic acid or the other builders mentioned below. Many builders are also bleach-stabilising agents by virtue of their ability to complex metal ions.

Zeolite and carbonate (carbonate (including bicarbonate and sesquicarbonate) are preferred builders, with carbonates being particularly preferred.

The composition may contain as builder a crystalline aluminosilicate, preferably an alkali metal aluminosilicate, more preferably a sodium aluminosilicate. This is typically present at a level of less than 15 wt. %.

Aluminosilicates are materials having the general formula:



where M is a monovalent cation, preferably sodium.

These materials contain some bound water and are required to have a calcium ion exchange capacity of at least 50 mg CaO/g. The preferred sodium aluminosilicates contain 1.5-3.5 SiO_2 units in the formula above. They can be prepared readily by reaction between sodium silicate and sodium aluminate, as amply described in the literature. The ratio of surfactants to aluminosilicate (where present) is preferably greater than 5:2, more preferably greater than 3:1.

Alternatively, or additionally to the aluminosilicate builders, phosphate builders may be used. In this art the term 'phosphate' embraces diphosphate, triphosphate, and phosphonate species. Other forms of builder include silicates, such as soluble silicates, metasilicates, layered silicates (e.g. SKS-6 from Hoechst).

If a laundry detergent, then preferably the laundry detergent formulation is a non-phosphate built laundry detergent formulation, i.e., contains less than 1 wt.% of phosphate. Most preferably the laundry detergent formulation is not built i.e. contain less than 1 wt.% of builder.

Chelating Agent

Chelating agents may be present or absent from the detergent compositions.

If present, then the chelating agent is present at a level of from 0.01 to 5 wt. %.

Example phosphonic acid (or salt thereof) chelating agents are: 1-Hydroxyethylidene-1,1-diphosphonic acid (HEDP); Diethylenetriaminepenta(methylenephosphonic acid) (DTPMP); Hexamethylenediaminetetra(methylenephosphonic acid) (HDTMP);

- 5 Aminotris(methylenephosphonic acid) (ATMP); Ethylenediaminetetra(methylenephosphonic acid) (EDTMP); Tetramethylenediaminetetra(methylenephosphonic acid) (TDTMP); and, Phosphonobutanetricarboxylic acid (PBTC).

Fluorescent Agent

- 10 The composition preferably comprises a fluorescent agent (optical brightener). Fluorescent agents are well known, and many such fluorescent agents are available commercially. Usually, these fluorescent agents are supplied and used in the form of their alkali metal salts, for example, the sodium salts.

- 15 The total amount of the fluorescent agent or agents used in the composition is generally from 0.0001 to 0.5 wt.%, preferably 0.005 to 2 wt.%, more preferably 0.01 to 0.1 wt.%.

Preferred classes of fluorester are: Di-styryl biphenyl compounds, e.g. Tinopal (Trade Mark) CBS-X, Di-amine stilbene di-sulphonic acid compounds, e.g. Tinopal DMS pure Xtra and
20 Blankophor (Trade Mark) HRH, and Pyrazoline compounds, e.g. Blankophor SN.

Preferred fluoresters are fluoresters with CAS-No 3426-43-5; CAS-No 35632-99-6; CAS-No 24565-13-7; CAS-No 12224-16-7; CAS-No 13863-31-5; CAS-No 4193-55-9; CAS-No 16090-02-1; CAS-No 133-66-4; CAS-No 68444-86-0; CAS-No 27344-41-8.

25

Most preferred fluoresters are: sodium 2 (4-styryl-3-sulphophenyl)-2H-naphthol[1,2-d]triazole, disodium 4,4'-bis{[(4-anilino-6-(N methyl-N-2 hydroxyethyl) amino 1,3,5-triazin-2-yl)]amino}stilbene-2-2' disulphonate, disodium 4,4'-bis{[(4-anilino-6-morpholino-1,3,5-triazin-2-yl)]amino} stilbene-2-2' disulphonate, and disodium 4,4'-bis(2-sulphostyryl)biphenyl.

30

The aqueous solution used in the method has a fluorester present. The fluorester is present in the aqueous solution used in the method preferably in the range from 0.0001 g/l to 0.1 g/l, more preferably 0.001 to 0.02 g/l.

Perfume

The composition preferably comprises a perfume. Many suitable examples of perfumes are provided in the CTFA (Cosmetic, Toiletry and Fragrance Association) 1992 International Buyers Guide, published by CFTA Publications and OPD 1993 Chemicals Buyers Directory
5 80th Annual Edition, published by Schnell Publishing Co.

Preferably the perfume comprises at least one note (compound) from: alpha-isomethyl ionone, benzyl salicylate; citronellol; coumarin; hexyl cinnamal; linalool; pentanoic acid, 2-methyl-, ethyl ester; octanal; benzyl acetate; 1,6-octadien-3-ol, 3,7-dimethyl-, 3-acetate;
10 cyclohexanol, 2-(1,1-dimethylethyl)-, 1-acetate; delta-damascone; beta-ionone; verdyol acetate; dodecanal; hexyl cinnamic aldehyde; cyclopentadecanolide; benzeneacetic acid, 2-phenylethyl ester; amyl salicylate; beta-caryophyllene; ethyl undecylenate; geranyl anthranilate; alpha-irone; beta-phenyl ethyl benzoate; alpa-santalol; cedrol; cedryl acetate; cedryl formate; cyclohexyl salicylate; gamma-dodecalactone; and, beta phenylethyl phenyl
15 acetate.

Useful components of the perfume include materials of both natural and synthetic origin. They include single compounds and mixtures. Specific examples of such components may be found in the current literature, e.g., in Fenaroli's Handbook of Flavour Ingredients, 1975,
20 CRC Press; Synthetic Food Adjuncts, 1947 by M. B. Jacobs, edited by Van Nostrand; or Perfume and Flavour Chemicals by S. Arctander 1969, Montclair, N.J. (USA).

It is commonplace for a plurality of perfume components to be present in a formulation. In the compositions of the present invention it is envisaged that there will be four or more,
25 preferably five or more, more preferably six or more or even seven or more different perfume components.

In perfume mixtures preferably 15 to 25 wt% are top notes. Top notes are defined by Poucher (Journal of the Society of Cosmetic Chemists 6(2):80 [1955]). Preferred top-notes
30 are selected from citrus oils, linalool, linalyl acetate, lavender, dihydromyrcenol, rose oxide and cis-3-hexanol.

The International Fragrance Association has published a list of fragrance ingredients (perfumes) in 2011. (<http://www.ifraorg.org/en-us/ingredients#.U7Z4hPIdWzk>)

The Research Institute for Fragrance Materials provides a database of perfumes (fragrances) with safety information.

Perfume top note may be used to cue the whiteness and brightness benefit of the invention.

5

Some or all of the perfume may be encapsulated, typical perfume components which it is advantageous to encapsulate, include those with a relatively low boiling point, preferably those with a boiling point of less than 300, preferably 100-250 Celsius. It is also advantageous to encapsulate perfume components which have a low CLog P (ie. those which will have a greater tendency to be partitioned into water), preferably with a CLog P of less than 3.0. These materials, of relatively low boiling point and relatively low CLog P have been called the "delayed blooming" perfume ingredients and include one or more of the following materials: allyl caproate, amyl acetate, amyl propionate, anisic aldehyde, anisole, benzaldehyde, benzyl acetate, benzyl acetone, benzyl alcohol, benzyl formate, benzyl
10 iso valerate, benzyl propionate, beta gamma hexenol, camphor gum, laevo-carvone, d-carvone, cinnamic alcohol, cinamyl formate, cis-jasmone, cis-3-hexenyl acetate, cuminic alcohol, cyclal c, dimethyl benzyl carbinol, dimethyl benzyl carbinol acetate, ethyl acetate, ethyl aceto acetate, ethyl amyl ketone, ethyl benzoate, ethyl butyrate, ethyl hexyl ketone, ethyl phenyl acetate, eucalyptol, eugenol, fenchyl acetate, flor acetate (tricyclo
20 decenyl acetate) , frutene (tricyclo decenyl propionate) , geraniol, hexenol, hexenyl acetate, hexyl acetate, hexyl formate, hydratropic alcohol, hydroxycitronellal, indone, isoamyl alcohol, iso menthone, isopulegyl acetate, isoquinolone, ligustral, linalool, linalool oxide, linalyl formate, menthone, menthyl acetphenone, methyl amyl ketone, methyl anthranilate, methyl benzoate, methyl benyl acetate, methyl eugenol, methyl heptenone, methyl heptene
25 carbonate, methyl heptyl ketone, methyl hexyl ketone, methyl phenyl carbiny acetate, methyl salicylate, methyl-n-methyl anthranilate, nerol, octalactone, octyl alcohol, p-cresol, p-cresol methyl ether, p-methoxy acetophenone, p-methyl acetophenone, phenoxy ethanol, phenyl acetaldehyde, phenyl ethyl acetate, phenyl ethyl alcohol, phenyl ethyl dimethyl carbinol, prenyl acetate, propyl bornate, pulegone, rose oxide, safrole, 4-terpinenol, alpha-
30 terpinenol, and /or viridine. It is commonplace for a plurality of perfume components to be present in a formulation. In the compositions of the present invention it is envisaged that there will be four or more, preferably five or more, more preferably six or more or even seven or more different perfume components from the list given of delayed blooming perfumes given above present in the perfume.

35

Another group of perfumes with which the present invention can be applied are the so-called 'aromatherapy' materials. These include many components also used in perfumery, including components of essential oils such as Clary Sage, Eucalyptus, Geranium, Lavender, Mace Extract, Neroli, Nutmeg, Spearmint, Sweet Violet Leaf and Valerian.

5

It is preferred that the laundry treatment composition does not contain a peroxygen bleach, e.g., sodium percarbonate, sodium perborate, and peracid.

Shading Dye

- 10 Preferably when the composition is a laundry detergent composition, then it comprises a shading dye. Preferably the shading dye is present at from 0.0001 to 0.1 wt.% of the composition.

- 15 Dyes are described in *Color Chemistry Synthesis, Properties and Applications of Organic Dyes and Pigments*, (H Zollinger, Wiley VCH, Zürich, 2003) and, *Industrial Dyes Chemistry, Properties Applications*. (K Hunger (ed), Wiley-VCH Weinheim 2003).

- Shading Dyes for use in laundry compositions preferably have an extinction coefficient at the maximum absorption in the visible range (400 to 700nm) of greater than
20 5000 L mol⁻¹ cm⁻¹, preferably greater than 10000 L mol⁻¹ cm⁻¹. The dyes are blue or violet in colour.

Preferred shading dye chromophores are azo, azine, anthraquinone, and triphenylmethane.

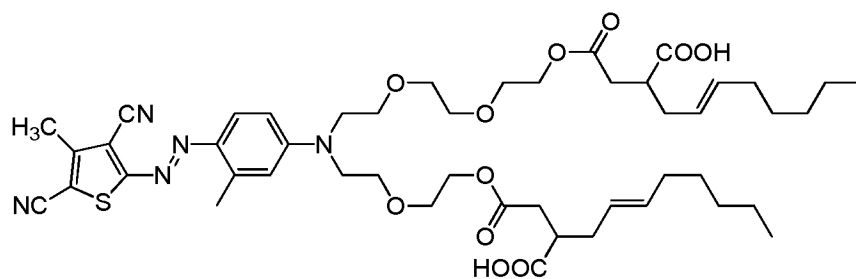
- 25 Azo, anthraquinone, phthalocyanine and triphenylmethane dyes preferably carry a net anionic charged or are uncharged. Azine preferably carry a net anionic or cationic charge. Blue or violet shading dyes deposit to fabric during the wash or rinse step of the washing process providing a visible hue to the fabric. In this regard the dye gives a blue or violet colour to a white cloth with a hue angle of 240 to 345, more preferably 250 to 320, most
30 preferably 250 to 280. The white cloth used in this test is bleached non-mercerised woven cotton sheeting.

Shading dyes are discussed in WO 2005/003274, WO 2006/032327(Unilever), WO 2006/032397(Unilever), WO 2006/045275(Unilever), WO 2006/027086(Unilever),

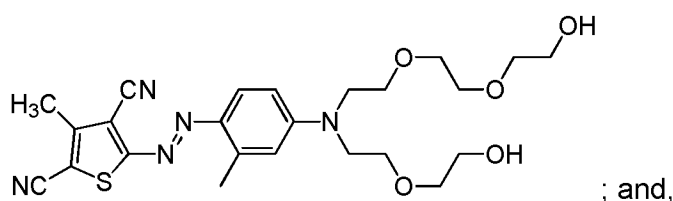
WO 2008/017570(Unilever), WO 2008/141880 (Unilever), WO 2009/132870(Unilever), WO 2009/141173 (Unilever), WO 2010/099997(Unilever), WO 2010/102861(Unilever), WO 2010/148624(Unilever), WO 2008/087497 (P&G), WO 2011/011799 (P&G), WO 2012/054820 (P&G), WO 2013/142495 (P&G) and WO 2013/151970 (P&G).

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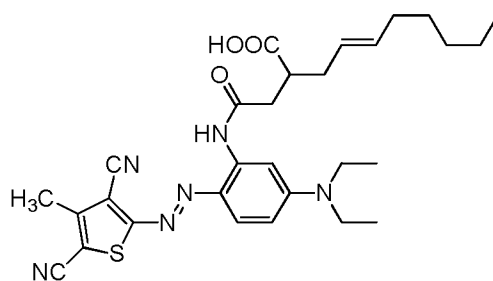
Mono-azo dyes preferably contain a heterocyclic ring and are most preferably thiophene dyes. The mono-azo dyes are preferably alkoxyated and are preferably uncharged or anionically charged at pH=7. Alkoxyated thiophene dyes are discussed in WO/2013/142495 and WO/2008/087497. Preferred examples of thiophene dyes are shown below:



10



; and,



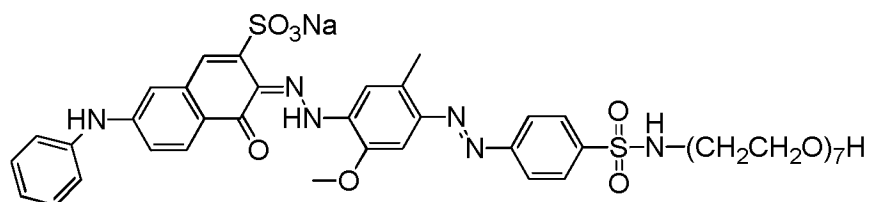
15

Bis-azo dyes are preferably sulphonated bis-azo dyes. Preferred examples of sulphonated bis-azo compounds are direct violet 7, direct violet 9, direct violet 11, direct violet 26, direct violet 31, direct violet 35, direct violet 40, direct violet 41, direct violet 51, Direct Violet 66, direct violet 99 and alkoxyated versions thereof. Alkoxyated bis-azo dyes are discussed in

20

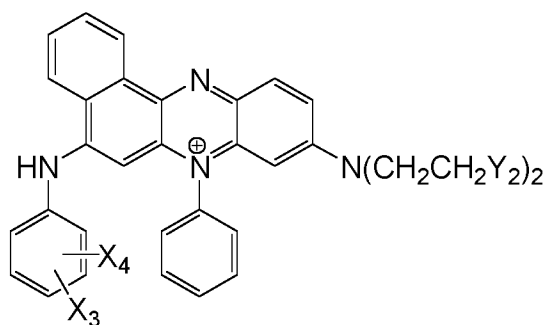
WO2012/054058 and WO2010/151906.

An example of an alkoxyated bis-azo dye is :



Thiophene dyes are available from Milliken under the tradenames of Liquitint Violet DD and
 5 Liquitint Violet ION.

Azine dye are preferably selected from sulphonated phenazine dyes and cationic phenazine dyes. Preferred examples are acid blue 98, acid violet 50, dye with CAS-No 72749-80-5, acid blue 59, and the phenazine dye selected from:



wherein:

X_3 is selected from: -H; -F; -CH₃; -C₂H₅; -OCH₃; and, -OC₂H₅;

X_4 is selected from: -H; -CH₃; -C₂H₅; -OCH₃; and, -OC₂H₅;

15 Y_2 is selected from: -OH; -OCH₂CH₂OH; -CH(OH)CH₂OH; -OC(O)CH₃; and, C(O)OCH₃.

The shading dye is present in the composition in range from 0.0001 to 0.5 wt %, preferably 0.001 to 0.1 wt%. Depending upon the nature of the shading dye there are preferred ranges depending upon the efficacy of the shading dye which is dependent on
 20 class and particular efficacy within any particular class. As stated above the shading dye is a blue or violet shading dye.

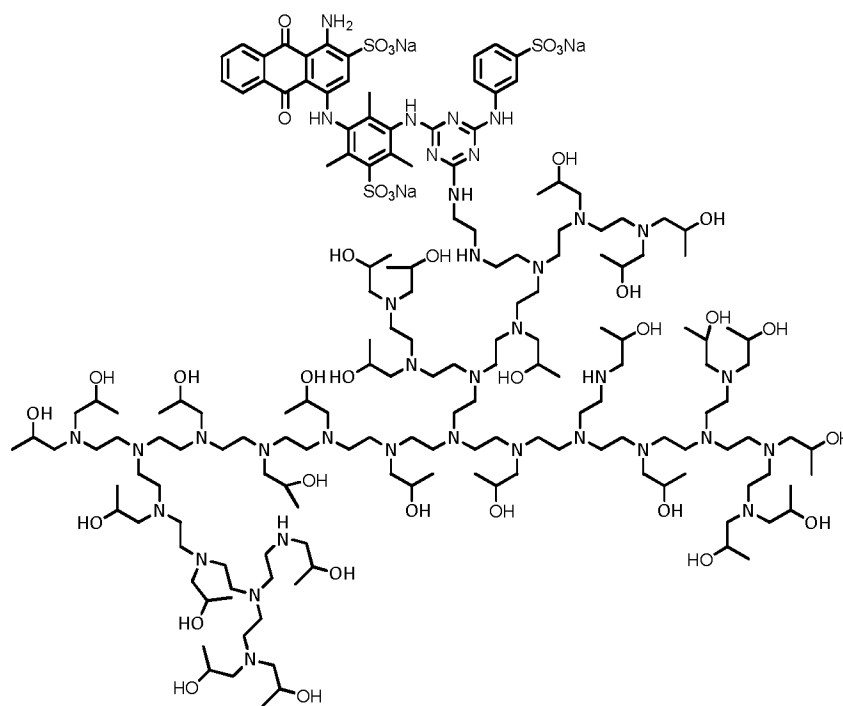
A mixture of shading dyes may be used.

25 The shading dye is most preferably a reactive blue anthraquinone dye covalently linked to an alkoxyated polyethyleneimine. The alkoxylation is preferably selected from ethoxylation and

propoxylation, most preferably propoxylation. Preferably 80 to 95 mol% of the N-H groups in the polyethylene imine are replaced with iso-propyl alcohol groups by propoxylation. Preferably the polyethylene imine before reaction with the dye and the propoxylation has a molecular weight of 600 to 1800.

5

An example structure of a preferred reactive anthraquinone covalently attached to a propoxylated polyethylene imine is:



(Structure I).

10

Polymers

The composition may comprise one or more further polymers. A preferred detergent composition comprises from 0.1 to 20 wt.%, preferably from 0.5 to 15 wt.% or one or more polymers. Examples are carboxymethylcellulose, poly (ethylene glycol), poly(vinyl alcohol), polycarboxylates such as polyacrylates, maleic/acrylic acid copolymers and lauryl methacrylate/acrylic acid copolymers.

15

Examples

The invention will be demonstrated by the following non-limiting examples.

20

Saponin (Escin), the saponin extract from horse chestnut (*Aesculus hippocastanum*) was purchased from Aldrich and used as supplied. The alkyl ether carboxylate was Emulsogen COL100 supplied by Clariant, it is oleyl based with 10 moles of ethoxylation.

- 5 An aqueous liquid detergent formulation was created containing 6 wt.% of Saponin. This was added to 26 French hard water to give an aqueous solution containing 4g/L of Saponin.

25g of the solution was decanted into a 125ml glass bottle without the creation of any foam. A lid was placed on the bottle and it was carefully placed on its axis on an orbital shaker and
 10 rotated at 200 rpm for 30 seconds. The bottle was removed and stood on a flat surface and the foam height measured, as the distance from the top of the liquid to the top of the foam.

The experiment was repeated but using 6 wt.% Alkyl Ether Carboxylate (AEC). All experiments were repeated eight times and these reference results shown in the table
 15 below.

	Foam height in cm	95% confidence
Saponin	36.500	2.095
AEC	17.250	1.095

From these results a mixture of AEC and RL would be expected to have a foam height of

$$\text{Foam height} = 36.5 - 0.1925 * (\% \text{AEC})$$

- 20 Where %AEC is the percent of AEC in the mixture.

The experiment was repeated with mixtures of AEC and Saponin and the experimental and expected foam heights given in the table below. These experiments were performed in quadruplet.

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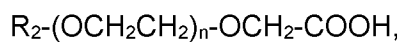
%AEC	%Saponin	Expected foam height	Measured foam height	95% confidence
10	90	34.6	22.5	1.6
25	75	31.7	19.5	0.9
75	25	22.1	15.5	1.0

The combination of AEC and Saponin produces much lower levels of foam than expected from the individual components.

CLAIMS

1. A cleaning composition comprising:

- (i) from 0.1 to 40 wt.%, preferably from 0.25 to 30 wt.%, more preferably from 0.5 to 25 wt.%, more preferably from 0.5 to 20 wt.%, most preferably from 0.5 to 15 wt.%, of a saponin; and,
- (ii) from 0.1 to 20 wt.% of an alkyl ether carboxylic acid surfactant of the following structure:



wherein:

R_2 is selected from saturated and mono-unsaturated C_{10} to C_{20} linear or branched alkyl chains, preferably selected from: C_{12} ; C_{14} ; C_{16} ; and, C_{18} linear alkyl chains, wherein n is selected from 5 to 30, preferably from 6 to 20, more preferably from 8 to 16,

and wherein the weight fraction of alkyl ether carboxylic acid to saponin is from 0.05 to 10, preferably from 0.1 to 3.

2. A composition according to claim 1, wherein the composition comprises from 0.5 to 6 wt.%, more preferably from 1 to 6 wt.%, most preferably from 2 to 6 wt.% of the alkyl ether carboxylic acid anionic surfactant.

3. A composition according to claim 1 or claim 2, wherein the alkyl chain, the R_2 group, of the alkyl ether carboxylic acid anionic surfactant is selected from saturated and mono-unsaturated C_{16} to C_{18} linear alkyl chains.

4. A composition according to any preceding claim, wherein the saponin has a triterpenoid backbone, and one or more sugar moieties attached to the triterpenoid backbone.

5. A composition according to claim 4, wherein the saponin has a triterpenoid backbone, and two or more sugar moieties attached to the triterpenoid backbone.

6. A composition according to any preceding claim, wherein the composition comprises from 1 to 60 wt.%, preferably from 2.5 to 50 wt.%, more preferably from 4 to 40 wt.%,

most preferably from 8 to 35 wt.% of a surfactant, said surfactant not including saponin.

- 5 7. A composition according to claim 6, wherein the surfactant composition comprises anionic and/or nonionic surfactant, preferably comprising both anionic and nonionic surfactant.
- 10 8. A composition according to any preceding claim, wherein the composition is a laundry detergent composition, preferably the laundry detergent composition is a liquid, gel or a powder, more preferably the laundry detergent is a liquid detergent, most preferably an aqueous laundry detergent composition.
- 15 9. A laundry detergent composition according to claim 8, wherein the laundry detergent composition comprises an alkoxylated polyamine, preferably at a level of from 0.1 to 8 wt.%, more preferably from 0.2 to 6 wt.%, most preferably from 0.5 to 5 wt.%, preferably the alkoxylated polyamine is an alkoxylated polyethylenimine, and/or alkoxylated polypropylenimine, more preferably the alkoxylation is ethoxylation or propoxylation or a mixture of both.
- 20 10. A laundry detergent composition according to claim 8 or claim 9, wherein the laundry detergent composition comprises a soil release polymer, preferably at a level of from 0.1 to 8 wt.%, more preferably from 0.2 to 6 wt.%, most preferably from 0.5 to 5 wt.%, preferably the soil release polymer is a polyester soil release polymer.
- 25 11. A detergent composition according to any preceding claim, additionally comprising one or more enzymes selected from lipases, proteases, amylases, cellulases, and mixtures thereof.
- 30 13. A composition according to any preceding claim, wherein when a liquid laundry detergent, the laundry detergent composition when dissolved in demineralised water at 4g/L, 293K has a pH of from 6 to 11, more preferably from 7 to 9.
- 35 14. A domestic method of treating a textile, the method comprising the steps of:
 - a) treating a textile with from 1 g/L of an aqueous solution of the cleaning composition as defined in any one of claims 1 to 13; and,

- b) allowing said aqueous solution to remain in contact with the textile for a time period of from 10 minutes to 2 days, then rinsing and drying the textile.

- 5 15. Use of a combination of saponin and alkyl ether carboxylic acid surfactant in a detergent composition to provide reduced foam levels compared to expected foam levels in a detergent composition, wherein the weight fraction of alkyl ether carboxylic acid to saponin is from 0.05 to 10, preferably from 0.1 to 3.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2021/056927

A. CLASSIFICATION OF SUBJECT MATTER INV. C11D1/06 C11D1/36 C11D3/00 C11D11/00 C11D17/00 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C11D		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 1 065 880 A (KU AILIAN [CN]) 4 November 1992 (1992-11-04)	1-15
Y	page 6, paragraph 2; claims -----	1,14,15
Y	WO 2015/191434 A2 (STEPAN CO [US]) 17 December 2015 (2015-12-17) claims; examples -----	1,14,15
Y	JP 2012 017286 A (ASAHI KASEI CHEMICALS CORP) 26 January 2012 (2012-01-26) paragraphs [0084], [0085], [0090]; claims; examples -----	1,14,15
Y	WO 2019/219302 A1 (UNILEVER PLC [GB]; UNILEVER NV [NL]; CONOPCO INC D/B/A UNILEVER [US]) 21 November 2019 (2019-11-21) claims; examples -----	1,14,15
☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents :		
"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family	
Date of the actual completion of the international search 9 June 2021	Date of mailing of the international search report 21/06/2021	
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Schoenhentz, Jérôme	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2021/056927

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