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(54) **LIQUID DETERGENT COMPOSITION COMPRISING KERATIN**

(57) The present invention relates to a liquid detergent composition that comprises a surfactant system comprising at least one anionic surfactant, at least one amphoteric/zwitterionic surfactant and keratin. The invention further relates to methods for washing of textiles using the detergents of the invention.

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Description

[0001] The present invention relates to a liquid detergent composition that comprises a surfactant system comprising at least one anionic surfactant, at least one amphoteric/zwitterionic surfactant and keratin. The invention further relates to methods for washing of textiles using the detergents of the invention.

[0002] Liquid detergent compositions are well-known in the art and widely used. Over recent years, the have become more and more popular with the consumers because they offer a number of advantages over solid compositions, including, for example, the ease of dosing, dispensing and dissolving into a laundering liquor. In addition, they are perceived to be safer and less harsh to the textiles and environment compared to solid compositions. In particular for laundering colored fabrics they have gained popularity ever since their introduction on the market.

[0003] In particular for washing colored fabrics, in particular black fabrics, it is important that the color is preserved during multiple washing cycles. Current widely available and market dominating powder detergents negatively impact both the color of the garments as well as fabric durability which is technically reflected by tensile strength loss.

[0004] There is thus need in the art for liquid detergent compositions that satisfy the consumers' needs with respect to textile color preservation while at the same time having fabric care properties that allow maintaining fabric durability and elasticity for multiple washing cycles.

[0005] It has now been found by the inventors that a liquid detergent composition that comprises a surfactant system comprising anionic surfactants and betaines in combination with keratin provide good fabric and color care and additionally maintaining fabric tensile strength.

[0006] In a first aspect, the present invention therefore relates to a liquid detergent composition, in particular an aqueous liquid detergent composition, that comprises

(A) a surfactant system comprising (A1) at least one anionic surfactant and (A2) at least one amphoteric/zwitterionic surfactant; and
(B) at least one keratin.

[0007] In a further aspect, the invention relates to methods for cleaning textiles, wherein the liquid detergent composition of the present invention is used.

[0008] "At least one", as used herein, relates to one or more, i.e. 1, 2, 3, 4, 5, 6, 7, 8, 9, or more. If used in combination with a compound, the term does not relate to the absolute number of molecules but rather to the number of different types of said compound. "At least one alkyl ether sulfate" thus means that at least one type but that also 2 or more different alkyl ether sulfate types can be present.

[0009] If not indicated otherwise, all percentages are by weight relative to the total weight of the composition.

[0010] "Liquid", as used herein the context of the detergent compositions, relates to compositions that are liquid under standard conditions, i.e. 20°C and 1013 mbar. The term covers all compositions that are pourable under these conditions and also covers gels and pastes and compositions having a yield point.

[0011] "Free of", as used herein in relation to a specific type of component, means that the referenced composition does not contain more than 0.5 wt.%, preferably no more than 0.1 wt.%, more preferably no more than 0.05 wt.% of said component relative to the total weight of the composition. Most preferably, said component is not contained at all.

[0012] The detergent compositions of the present invention can be used as detergents for textiles, carpets or natural fibers, but are preferably laundry detergents. In various embodiments, the detergents disclosed herein are heavy duty liquid (HDL) detergents.

[0013] The detergent compositions of the invention comprise a surfactant system, wherein said surfactant system comprises at least one anionic surfactant and at least one amphoteric/zwitterionic surfactant. The term "surfactant system" as used herein, refers to the totality of all surfactants comprised in the liquid detergent compositions of the invention.

[0014] In various embodiments, the anionic surfactant includes an alkyl ether sulfate. Preferred alkyl ether sulfates are those of formula (I)

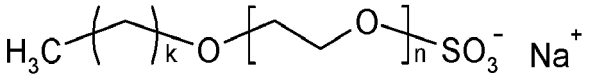
$$R^1\text{-}O\text{-}(AO)_n\text{-}SO_3^-\ X^+ \qquad (I).$$

In formula (I) R^1 represents a linear or branched, substituted or unsubstituted alkyl group, preferably a linear, unsubstituted alkyl group, more preferably a fatty alcohol moiety. Preferred R^1 moieties are selected from the group consisting of decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl moieties and mixtures thereof, wherein those groups with an even number of carbon atoms are preferred. Particularly preferred R^1 moieties are derived from C_{10}-C_{18} fatty alcohols, such as those derived from coconut oil alcohols, tallow fatty alcohols, lauryl, myristyl, cetyl or stearyl alcohol or from C_{10}-C_{20} oxoalcohols.

[0015] AO represents an ethyleneoxide (EO) or propyleneoxide (PO) group, preferably an ethyleneoxide group. The

index n represents an integer from 1 to 50, preferably from 1 to 20 and more preferably from 1 to 10. Particularly preferably, n is 1, 2, 3, 4, 5, 6, 7 or 8. X represents a monovalent cation or the n-th part of an n-valent cation, preferred are alkali metal cations, specifically Na^+ and K^+, most preferably Na^+. Further cations X^+ may be selected from $NH4^+$, ½ Zn^{2+},½ Mg^{2+},½ Ca^{2+},½ Mn^{2+}, and combinations thereof.

[0016] In various preferred embodiments, the detergent compositions comprise an alkyl ether sulfate selected from fatty alcohol ether sulfates of formula (II)



(II)

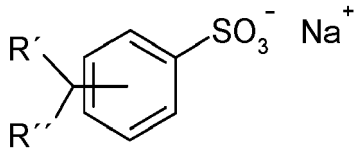
wherein k = 9 to 19, and n = 1, 2, 3, 4, 5, 6, 7 or 8. Preferred are C_{10-15} fatty alcohol ether sulfates with 1-7, more preferably 1-3 EO (k = 9-15, n = 1-7, 1-3), even more preferred the C_{12-14} fatty alcohol ether sulfates with 1-3, particularly 2 EO (k = 11-13, n = 1-3 or 2), more particularly the sodium salts thereof. Particularly preferred is lauryl ether sulfate sodium salt with 2 EO. The level of ethoxylation is an average value and can, for a specific compound, be an integer or fractional number.

[0017] The alkyl ether sulfate is contained in the compositions of the invention in an amount of 1.0 to 15.0 wt.-% relative to the total weight of the composition, preferably 1.5 to 10.0 wt.-%, more preferably 2.0 to 7.0 wt.-%, most preferably 3.0 to 6.0 wt.-%.

[0018] In various embodiments, the surfactant system comprises an alkyl benzene sulfonic acid or salt thereof (sulfonate). In various embodiments, such an alkyl benzene sulfonic acid or salt thereof (sulfonate) is further comprised in the detergent composition in addition to the alkyl ether sulfate described above.

[0019] In the following reference is made to the respective sulfonates, but it is understood that the corresponding free acids may also be used and optionally neutralized during pH adjustment of the detergent composition.

[0020] Exemplary alkyl benzene sulfonates include, but are not limited to linear and branched alkyl benzene sulfonates, preferably linear alkyl benzene sulfonates. Exemplary compounds are those of formula (III)



(III),

wherein R' and R" are independently H or alkyl and combined comprise 9 to 19, preferably 9 to 15 and more preferably 9 to 13 or 10 to 13 carbon atoms. Particularly preferred are dodecyl and tridecyl benzene sulfonates, in particular the free acids or sodium salts thereof. Preferred contents range from 1.0 to 8.0 wt.-%, preferably 1.0 to 5.0 wt.-%, more preferably 1.5 to 4.0 wt.-% relative to the total weight of the composition.

[0021] In various embodiments of the invention, the liquid detergent compositions comprise both an alkyl ether sulfate and an alkyl benzene sulfonate, as defined herein.

[0022] In various embodiments, the liquid detergent composition may comprise further anionic surfactants. Suitable surfactants are known to those skilled in the art.

[0023] The liquid detergent compositions of the invention further comprise an amphoteric/zwitterionic surfactant, preferably a betaine.

[0024] Suitable betaines comprise but are not limited to alkylbetaines, alkylamidobetaines, imidazoliniumbetaines, sulfobetaines (INCI: Sultaines) as well as phosphobetaines. In various embodiments, the betaines are compounds of formula (IV),

$$R^1\text{-}[CO\text{-}X\text{-}(CH_2)_n]_x\text{-}N^+(R^2)(R^3)\text{-}(CH_2)_m\text{-}[CH(OH)\text{-}CH_2]_y\text{-}Y^- \qquad (IV)$$

wherein

R^1 represents a saturated or unsaturated C_{6-22}-alkyl group, preferably C_{8-18}-alkyl group, more preferably a saturated C_{10-16}-alkyl group, for example a saturated C_{12-14}-alkyl group,
X represents NH, NR^4 with R^4 being C_{1-4}-alkyl, O or S,
n represents an integer from 1 to 10, preferably 2 to 5, more preferably 3,
x is 0 or 1, preferably 1,

R^2, R^3 represent independent from each other C_{1-4}-alkyl, optionally hydroxy-substituted, preferably methyl,
m represents an integer from 1 to 4, preferably 1, 2 or 3,
y is 0 or 1, and
Y represents COO, SO_3, $OPO(OR^5)O$ or $P(O)(OR^5)O$, wherein R^5 represents H or a C_{1-4}-alkyl group.

[0025] Alkyl- and alkylamidobetaines, i.e. betaines of formula (IV) with a carboxylic acid group (Y- = COO^-), are so-called carbobetaines.

[0026] Preferred betaines are alkylbetaines of formula (IVa), alkylamido betaines of formula (IVb), sulfobetaines of formula (IVc) and amidosulfobetaines of formula (IVd),

$$R^1\text{-}N^+(CH_3)_2\text{-}CH_2COO^- \quad \text{(IVa)}$$

$$R^1\text{-}CO\text{-}NH\text{-}(CH_2)n\text{-}N^+(CH_3)_2\text{-}CH_2COO^- \quad \text{(IVb)}$$

$$R^1\text{-}N^+(CH_3)_2\text{-}CH_2CH(OH)CH_2SO_3^- \quad \text{(IVC)}$$

$$R^1\text{-}CO\text{-}NH\text{-}(CH_2)_3\text{-}N^+(CH_3)_2\text{-}CH_2CH(OH)CH_2SO_3^- \quad \text{(IVd)},$$

wherein R^1 is defined as in formula (IV).

[0027] Particularly preferred are carbobetaines, such as the carbobetaines of formulae (IVa) and (IVb), most preferred are the alkylamidobetaines of formula (IVb), in particular those with n=2-4, preferably 3, and R^1 = C_{8-18} alkyl, preferably C_{12-14} alkyl.

[0028] Particularly preferred are cocoamidopropylbetaines (CAPB), which are for example commercially available under the tradename Tego® Natural Betaine from Evonik.

[0029] Preferred contents of the amphoteric/zwitterionic surfactant, preferably the betaine, range from 0.1 to 5.0 wt.-%, preferably 0.2 to 3.0 wt.-%, more preferably 0.2 to 2.0 wt.-% relative to the total weight of the composition.

[0030] In addition, the compositions of the invention may comprise one or more nonionic surfactants.

[0031] Preferred nonionic surfactants are those of formula (V)

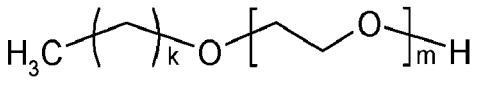
$$R^2\text{-}O\text{-}(AO)_m\text{-}H \quad \text{(V)},$$

wherein R^2 represents a linear or branched substituted or unsubstituted alkyl moiety, AO represents an ethylene oxide (EO) or propylene oxide (PO) group and m is an integer from 1 to 50.

[0032] In formula (V) R^2 preferably represents a linear or branched, substituted or unsubstited alkyl group, preferably a linear, unsubstituted alkyl group, particularly preferred a fatty alcohol group. Preferred groups are R^2 are selected from decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl groups and combinations thereof, wherein those groups with an even number of carbon atoms are preferred. Particularly preferred are R^2 groups derived from C_{12}-C_{18} fatty alcohols, such as coconut oil alcohol, tallow oil alcohol, lauryl, myristyl, cetyl or stearyl alcohol or from C_{10}-C_{20} oxoalcohols.

[0033] AO represents an ethyleneoxide (EO) or propyleneoxide (PO) group, preferably an ethyleneoxide group. The index m represents an integer from 1 to 50, preferably from 1 to 20 and more preferably from 1 to 10. Particularly preferably, m is 3, 4, 5, 6, 7, or 8, most preferably 3-7.

[0034] In various preferred embodiments, the detergent compositions comprise an alkyl ether selected from fatty alcohol ethers of formula (VI)



(VI)

wherein k = 11 to 19, m = 1, 2, 3, 4, 5, 6, 7 or 8. Preferred are C_{12-18} fatty alcohols with 1-8 EO (k = 11-17, m = 1-8 in formula (V)). More preferred are C_{12-18} alcohols having 2-7 EO, most preferred are C_{12-18} or C_{12} alkyl ethers with 7 EO.

[0035] Such nonionic fatty alcohol ethoxylates may be contained in the formulation in amounts of 0.2 to 5.0 wt.-%, preferably 0.3. to 4.0 wt.-%, more preferably 0.5 to 3.0 wt.-%.

[0036] The detergents may further include other nonionic surfactants, such as alkyl glucosides of the general formula $RO(G)_x$, where R is a primary linear or 2-methyl-branched aliphatic radical containing 8 to 22 and preferably 12 to 18 carbon atoms and G stands for a glucose unit. The degree of oligomerization x, which indicates the distribution of monoglucosides and oligoglucosides, is a number of 1 to 10 and preferably a number of 1.2 to 1.4. However, in preferred

embodiments, the compositions do not include such alkyl glucosides.

[0037] In various embodiments, the surfactant system comprises at least two anionic surfactants, namely the at least one alkyl ether sulfate and preferably at least one alkyl benzene sulfonate, and at least one betaine and optionally at least one fatty alcohol ethoxylate. In these combinations of surfactants, the respective surfactants can be used in the above-described amounts.

[0038] The compositions may comprise, for example, 2.0 to 30.0, preferably 3.0 to 20.0 wt.-% of the surfactant system. Preferred are compositions that comprise 4.0 to 15.0 wt.-% surfactants. Said surfactant system may comprise or consist of anionic surfactants, preferably (1) 1.0 to 15.0 wt.-% relative to the total weight of the composition, preferably 1.5 to 10.0 wt.-%, more preferably 2.0 to 7.0 wt.-%, most preferably 3.0 to 6.0 wt.-% C_{10-16} alkyl ether sulfates with 1 to 7 EO, preferably C_{12-14} fatty alcohol ether sulfates with 1-3 EO, more preferably lauryl ether sulfate with 2 EO, (2) 1.0 to 8.0 wt.-%, preferably 1.0 to 5.0 wt.-%, more preferably 1.5 to 4.0 wt.-% of a (linear) alkyl benzene sulfonate, preferably dodecyl or tridecyl benzene sulfonate, and (3) 0.1 to 5.0 wt.-%, preferably 0.2 to 3.0 wt.-%, more preferably 0.2 to 2.0 wt.-% of a betaine, preferably CAPB, and, optionally (4) 0.2 to 5.0 wt.-%, preferably 0.3. to 4.0 wt.-%, more preferably 0.5 to 3.0 wt.-% C_{12-18} alkyl ethers with 1-8 EO, preferably C_{12-18} alkyl ethers having 2-7 EO, most preferably C_{12-18} alkyl ethers with 3-7 EO. All afore-mentioned percentages relate to the total weight of the composition.

[0039] The liquid detergent compositions further comprise at least one keratin. Keratin is a fibrous structural protein rich in cysteine residues and the key structural material making up scales, hair, nails, feathers, horns, claws, hooves, calluses and the outer layer of skin among vertebrates. In its natural form keratin is highly insoluble in water and most organic solvents. The keratin used in accordance with the present invention is a protein hydrolysate, i.e. keratin in hydrolyzed form (INCI: hydrolyzed keratin; CAS No. 69430-36-0). Such a keratin is, for example, commercially available under the tradename Nutrilan® Keratin W PP from BASF, SE.

[0040] The keratin (hydrolysate) may be comprised in the liquid detergent compositions in amounts of from 0.001 to 0.5 wt.-%, preferably in amounts of from 0.005 to 0.2 wt.-%, more preferably 0.01 to 0.1 or to 0.05 wt.-%, relative to the total weight of the composition.

[0041] For cold wash properties, it can be beneficial to additionally include soaps. In various embodiments, the detergent compositions comprise soaps in amounts of up to 1 wt.-%, preferably up to 0.5 wt.-% soaps.

[0042] The detergent compositions of the invention are preferably aqueous liquid compositions and as such comprise significant quantities of water, typically 20.0 to 95.0 wt.%, preferably 60.0 to 93.0 wt.%.

[0043] The detergent compositions of the invention may further comprise one or more enzymes. In various embodiments where the composition further comprises at least one enzyme, said at least one enzyme may be selected from the group consisting of proteases, amylases, lipases, cellulases, mannanases, pectinases and combinations thereof. In such embodiments, the composition may comprise 0.001 to 5 wt.-%, more preferably 0.001 to 3 wt.-%, enzymes relative to active protein and the total weight of the composition.

[0044] In various embodiments, the detergent composition comprises at least one cellulase, preferably in an amount of 0.001 to 0.3 wt.-% relative to active protein and the total weight of the composition.

[0045] The detergent compositions of the invention may further comprise a builder system. The builder system may be a phosphate-free builder system. However, the composition may comprise phosphonates. Accordingly, the term "phosphate-free", as used herein does not refer to phosphonates.

[0046] If the compositions comprise phosphonates, the phosphonates are preferably hydroxyalkane and/or amino alkane phosphonates, such as 1-hydroxyethane-1 ,1-diphosphonate (HEDP), ethylenediamine tetramethylene phosphonate (EDTMP), diethylenetriamine pentamethylene phosphonate (DTPMP), and lysine tetramethylene phosphonate (LTMP). If present, phosphonates are used in amounts of 0.1 to 10.0 wt.-%, preferably 0.5 to 8.0 Gew.-%, more preferably 0.1 to 1.5 wt.-%. The total phosphorus content of the detergents is preferably less than 0.5% by weight.

[0047] Suitable builders include, without limitation, inorganic builders, such as silicates, aluminosilicates (particularly zeolite), and carbonates, as well as organic builders, such as organic di- and polycarboxylic acids, aminocarboxylic acids and combinations thereof. Preferred in the liquid compositions of the invention are carbonates, di- and polycarboxylic acids and aminocarboxylic acids. Also suitable are alkali metal hydroxides, in particular sodium hydroxide, but these are, besides their use for pH control, not preferred.

[0048] Suitable carbonates include alkali metal carbonates, hydrogen carbonates and sesquicarbonates, with alkali metal carbonates, in particular sodium carbonate being preferred.

[0049] Suitable organic builders include polycarboxylic acids which can be used as free acids or in form of their salts, including, but not limited to, citric acid, adipic acid, succinic acid, glutaric acid, malic acid, tartric acid, maleic acid, fumaric acid, and sugar acids. In addition to their builder properties, the free acids can also be used for pH control. Preferred are citric acid, succinic acid, glutaric acid, adipic acid and gluconic acid, and combinations thereof. Particularly preferred is citric acid.

[0050] In addition or alternatively to the afore-mentioned builders, the compositions may also include aminocarboxylic acids or salts thereof, i.e. aminocarboxylates. In various embodiments, suitable aminocarboxylic acids/aminocarboxylates are selected from the group consisting of L-glutamic acid N,N-diacetic acid (GLDA), methyl glycine diacetic acid

(MGDA), imino disuccinic acid (IDS), ethylenediamine N,N'-disuccinic acid (EDDS), diethylenetriamine pentaacetic acid (DTPA), beta-alanine N,N-diacetic acid, hydroxyethylenediamine triacetic acid (HEDTA), and alkali metal salts thereof as well as combinations of any one of more of the afore-mentioned.

[0051] In various embodiments, the detergent compositions comprise a builder system comprising relative to the total weight of the composition 2.0 to 10.0 wt.-%, preferably 3.0 to 4.0 wt.-% citric acid or citrate, such as sodium citrate. Additionally, the builder system may comprise phosphonates in amounts of 0.1 to 1.5 wt.-%, in particular DTPMP or a sodium salt thereof.

[0052] Further organic builders include polymeric polycarboxylates, polyacetals, dextrins and others. In various embodiments, the builder system is comprised in the compositions in an amount of 3.0 to 15.0 wt.-%, preferably 4.0 to 10.0 wt.-%.

[0053] The pH value of the detergents according to the invention is generally in the range of from 7 to 12, preferably in the range from 7 to 10.5. Relatively high pH values, for example above 9, may be adjusted by the use of small quantities of sodium hydroxide or alkaline salts, such as sodium carbonate. The liquid detergents are typically transparent, translucent, or opaque, are flowable, and may be poured under the sole effect of gravity without any need for other shear forces to be applied. Their viscosity is generally in the range of 100-1000 mPas (Brookfield viscosimeter, spindle 2, 20 rpm, 20° C), preferably in the range of between 150 and 400 mPas.

[0054] In addition to the ingredients mentioned above, however, the detergents may commonly contain at least one, preferably two or more other substances selected from the group consisting of pH adjusting agents, pearlescent agents, perfumes, dyes, colorants, antimicrobial active substances, germicides, fungicides, antioxidants, preservatives, and softening compounds.

[0055] Further possible ingredients include silicone oils, anti-redeposition agents, anti-greying agents, shrinkage preventers, wrinkle protection agents, corrosion inhibitors, antistatic agents, bittering agents, ironing adjuvants, proofing and impregnation agents, swelling and anti-slip agents, complexing agents and UV absorbers.

[0056] Also included may be bleaching agents, bleach activators, and bleach catalysts, however, in various embodiments, the compositions are free of those.

[0057] The present invention further relates to methods for cleaning textiles, wherein the liquid detergent composition or a washing liquor containing the liquid detergent composition of the present invention contacts the textile in at least one method step. The methods are typically either carried out in an automatic washing machine or by hand.

[0058] Methods for cleaning of textiles are generally characterized by the fact that in several different process steps various cleaning-active substances are applied to the textiles and after the contact time said cleaning-active substances are washed off, or that the textiles are treated in any other way with a detergent or a solution of said substance.

[0059] All embodiments described herein in relation to the compositions of the invention are similarly applicable to the methods of the invention and vice versa.

Examples

Example 1: Formulation

[0060] The following formulation was made:

Table 1: Liquid detergent formulation (amounts in wt.-% relative to total weight)

Ingredient	**E1**
LAS, Na salt	2.3
Laurylethersulfate (LES), 2 EO	4.4
Cocoamidopropylbetaine (CAPB)	0.8
C_{12} Fatty alcohol ethoxylate, 7 EO	1.4
Soap	0.3
NaOH (50%)	0.72
NaCl	2.5
Keratin hydrolysate (Nutrilan® Keratin W PP)	0.02
Cellulase enzyme formulation (Biotouch® FCL75)	0.02
Glycerol	0.3

(continued)

Ingredient	E1
Perfume	0.7
Preservative (Acticide® 2550)	0.1
Opacifier (Acusol OP 301)	0.25
Water	Ad 100

Example 2: Color Care Test

[0061] Color Care was tested for inventive composition E1 at 30°C in a top load automatic washing machine against four commercially available liquid/powder detergent compositions (R1= Persil Black; R2= Ariel Powder; R3= Omino Black; R4 = Sepid Black) in an amount of 100 g each with water of 16° dH hardness over 20 washing cycles and colored cotton fabrics (black, green, red, blue) and rated from 1-5 with 1 being a major difference in color between washed and pre-wash and 5 being no difference between washed and pre-wash color. The following results were obtained:

	E1	R1	R2	R3	R4
Black	3,4	2,0	2,0	2,5	2,4
Green	3,3	2,6	2,2	2,7	2,7
Red	3,5	2,5	1,9	2,8	2,6
Blue	3,9	2,9	2,7	3,1	3,0

[0062] The results show that the inventive composition performs significantly better than all reference compositions with respect to color care.

Example 3: Antipilling Test

[0063] Antipilling was tested for inventive composition E1 at 30°C in a top load automatic washing machine against four commercially available liquid/powder detergent compositions (R1= Persil Black; R2= Ariel Powder; R3= Omino Black; R4 = Sepid Black) in an amount of 100 g each with water of 16° dH hardness over 20 washing cycles using a pilling monitor (94% cotton; 6% Elasthan) either new or in pre-pilled form and rated from 1-5 with 1 being major pilling and 5 being essentially no pilling. The following results were obtained:

	Initial value	E1	R1	R2	R3	R4
New monitor	5	4.3	2.5	2.3	2.6	2.1
Pre-pilled monitor	1	4.3	1.1	1.1	2.9	1.1

[0064] The results show that the inventive composition improves pilled fabrics and prevents pilling of new fabrics.

Example 4: Wash performance

[0065] Wash performance was tested for inventive composition E1 at 30°C in a top load automatic washing machine against two commercially available liquid/powder detergent compositions (R1= Persil Black; R2= Tide Black) in an amount of 100 g each with water of 16° dH hardness. Wash performance was tested on 54 commercially available stains. Using the liquid detergent of Example 1 (E1) as a benchmark, the cleaning performance on each stain was determined and rated as being "better" "equal" to or "worse" than the benchmark. The following results were obtained:

	R1	R2
Better	13	12
Equal	36	30

(continued)

	R1	R2
Worse	5	12

[0066] The results show that the inventive composition performs at least as good or even better on many stains compared to conventional liquid detergents used at 16° dH.

Example 5: Tensile Strength and foaming

[0067] Further experiments were conducted to compare foaming of the inventive composition and its influence on fabric tensile strength. It was found that the inventive compositions performs equal to currently marketed formulations with respect to foaming and provide for improved fabric tensile strength in Crepe (100 % PES), Jeans (80% Acetate, 20 % PES or 98% Cotton, 2% Elasthan) and Cotton (100% Cotton).

Claims

1. Liquid detergent composition, comprising

(A) a surfactant system comprising (A1) at least one anionic surfactant and (A2) at least one amphoteric/zwitterionic surfactant; and
(B) at least one keratin.

2. The liquid detergent composition according to claim 1, wherein the at least one anionic surfactant comprises at least one alkyl ether sulfate of formula (I) or the corresponding acid

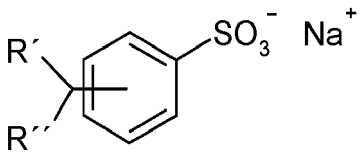
$$R^1\text{-}O\text{-}(AO)_n\text{-}SO_3^-\ X^+ \qquad (I)$$

wherein

R^1 represents a linear or branched, substituted or unsubstituted alkyl group, preferably a linear, unsubstituted alkyl group, more preferably a fatty alcohol moiety; most preferably a $C_{12\text{-}18}$ or $C_{12\text{-}14}$ or C_{12} alkyl moiety;
AO represents an ethyleneoxide (EO) or propyleneoxide (PO) group, preferably an ethyleneoxide group;
n represents an integer from 1 to 50, preferably from 1 to 20, more preferably from 1 to 10 and most preferably 2; and
X represents a monovalent cation or the n-th part of an n-valent cation, preferably an alkali metal cation, more preferably Na^+ or K^+, most preferably Na^+.

3. The liquid detergent composition according to claim 2, wherein the alkyl ether sulfate is comprised in the detergent composition in an amount of from 1.0 to 15.0 wt.-% relative to the total weight of the composition, preferably 1.5 to 10.0 wt.-%, more preferably 2.0 to 7.0 wt.-%, most preferably 3.0 to 6.0 wt.-%.

4. The liquid detergent composition according to any one of claims 1 to 3, wherein the at least one anionic surfactant comprises a linear or branched alkyl benzene sulfonate, preferably linear alkyl benzene sulfonate of formula (III)



(III),

wherein R' and R" are independently H or alkyl and combined comprise 9 to 19, preferably 9 to 15 and more preferably 9 to 13 or 10 to 13 carbon atoms.

5. The liquid detergent composition according to claim 4, wherein the alkyl benzene sulfonate is comprised in the

detergent composition in an amount of from 1.0 to 8.0 wt.-%, preferably 1.0 to 5.0 wt.-%, more preferably 1.5 to 4.0 wt.-% relative to the total weight of the composition

6. The liquid detergent composition according to any one of claims 1 to 5, wherein the at least one amphoteric/zwitterionic surfactant is a betaine, preferably cocamidopropylbetaine.

7. The liquid detergent composition according to claim 6, wherein the betaine is comprised in the detergent composition in an amount of from 0.1 to 5.0 wt.-%, preferably 0.2 to 3.0 wt.-%, more preferably 0.2 to 2.0 wt.-% relative to the total weight of the composition.

8. The liquid detergent composition according to any one of claims 1 to 7, wherein the detergent composition further comprises a nonionic surfactant, preferably a fatty alcohol alkoxylate, more preferably a fatty alcohol ethoxylate, optionally in an amount of from 0.2 to 5.0 wt.-%, preferably 0.3. to 4.0 wt.-%, more preferably 0.5 to 3.0 wt.-%.

9. The liquid detergent composition according to any one of claims 1 to 8, wherein the detergent composition further comprises soaps, optionally in amounts of up to 1 wt.-%, preferably up to 0.5 wt.-%.

10. The liquid detergent composition according to any one of claims 1 to 9, wherein the at least one keratin is a keratin hydrolysate.

11. The liquid detergent composition according to any one of claims 1 to 10, wherein the detergent compositions comprises the at least one keratin in an amount of from 0.001 to 0.5 wt.-%, preferably from 0.005 to 0.2 wt.-%, more preferably 0.01 to 0.1 or to 0.05 wt.-%, relative to the total weight of the composition.

12. The liquid detergent composition according to any one of claims 1 to 11, further comprising one or more enzymes, preferably selected from the group consisting of proteases, amylases, lipases, cellulases, mannanases, pectinases and combinations thereof, more preferably a cellulase.

13. The liquid detergent composition of any one of claims 1 to 12, wherein the detergent composition is an aqueous liquid composition and comprises water in an amount of from 20.0 to 95.0 wt.%, preferably 60.0 to 93.0 wt.%, relative to the total weight of the composition.

14. The liquid detergent composition of any one of claims 1 to 8, wherein the detergent composition further comprises at least one, preferably two or more other substances selected from the group consisting of pH adjusting agents, pearlescent agents, perfumes, dyes, colorants, antimicrobial active substances, germicides, fungicides, antioxidants, preservatives, and softening compounds.

15. Method for cleaning textiles, wherein the liquid detergent composition according to any one of claims 1 to 14 is used.

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EUROPEAN SEARCH REPORT

Application Number
EP 20 21 3868

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 2017/056305 A1 (SCHULZE ZUR WIESCHE ERIK [DE] ET AL) 2 March 2017 (2017-03-02) * paragraph [0133]; claim 10 * -----	1-3,6, 10,13,14	INV. C11D17/00 C11D1/94 C11D3/384
X	DATABASE WPI Week 201986 Thomson Scientific, London, GB; AN 2019-88911X XP002803125, & CN 110 354 041 A (INFINITUS CHINA CO LTD) 22 October 2019 (2019-10-22) * abstract * -----	1,6-8, 10,11, 13,14	C11D11/00 C11D1/22 C11D1/29 C11D1/90
X Y	DE 10 2017 120042 A1 (HENKEL AG & CO KGAA [DE]) 28 February 2019 (2019-02-28) * paragraphs [0016], [0019] - [0026]; claims; examples 1-B; tables 1, 4, 5 * -----	1-5,8-15 6,7	
Y	EP 2 607 469 A1 (UNILEVER PLC [GB]) 26 June 2013 (2013-06-26) * claims 1-10; table 1 * -----	6,7	
T	DATABASE ChemIDplus [Online] U.S National Library of Medicine; 5 February 2019 (2019-02-05), "Substance Name: Cocodimonium hydroxypropyl hydrolyzed keratin (1000 MW)", XP002803039, Database accession no. RN: 151248-07-6 * abstract * -----		

TECHNICAL FIELDS SEARCHED (IPC)
C11D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	28 May 2021	Loiselet-Taisne, S

CATEGORY OF CITED DOCUMENTS

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28-05-2021

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2017056305 A1	02-03-2017	DE 102015216687 A1	02-03-2017
		FR 3040299 A1	03-03-2017
		GB 2547061 A	09-08-2017
		US 2017056305 A1	02-03-2017
		US 2019282475 A1	19-09-2019
CN 110354041 A	22-10-2019	NONE	
DE 102017120042 A1	28-02-2019	NONE	
EP 2607469 A1	26-06-2013	NONE	

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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Non-patent literature cited in the description

- *CHEMICAL ABSTRACTS,* 69430-36-0 **[0039]**