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(54) **LIQUID LAUNDRY DETERGENT COMPOSITION**

FLÜSSIGE WASCHMITTELZUSAMMENSETZUNG

COMPOSITION DÉTERGENTE LIQUIDE POUR LE LAVAGE

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(56) References cited:
**WO-A1-2016/180552 WO-A1-2017/054983
WO-A1-2017/174252 DE-A1-102013 218 614**
• **Anonymous: "AKYPO", Kao Chemicals , 23
March 2016 (2016-03-23), XP002774209,
Retrieved from the Internet:
URL:<https://web.archive.org/web/20160823043716/http://chemical.kao.com/global/products/productname/c040103.html> [retrieved on
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EP 3 622 047 B1

Description**FIELD OF INVENTION**

[0001] The present invention provides a laundry detergent composition. In particular the invention relates to an aqueous liquid laundry detergent composition for use in domestic laundry.

BACKGROUND OF THE INVENTION

[0002] Aqueous domestic laundry liquid formulations containing alkyl ether carboxylates in combination with other anionic surfactants as the main surfactants are known. Alkyl ether carboxylates enhance the cleaning performance of the detergent and it is desired to maximise this enhancement.

[0003] WO 2016/180552 (Unilever) discloses enzymatic and dispersant formulation for use in domestic laundry comprising alkyl ether carboxylic acid, protease, anionic surfactant and optional nonionic surfactant. Exemplified are formulations comprising alkyl ether carboxylates along with a surfactant system that comprises linear alkyl benzene sulfonate, nonionic surfactant and sodium laureth ether sulfate in weight ratios of 4:1:5.

[0004] DE 102013218614 (Henkel) discloses a liquid detergent formulation containing a surfactant mixture comprising at least one ether carboxylate, with improved cleaning performance, especially on greasy stains and / or at low temperatures. Exemplified are formulations comprising alkyl ether carboxylates along with a surfactant system that comprises linear alkyl benzene sulfonate, nonionic surfactant and laureth ether sulfate in weight ratios of 4:2:5.

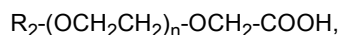
[0005] WO 2017/054983 (Unilever) discloses liquid detergents comprising LAS, SLES (3EO) and alkyl ether carboxylates. Preferred alkyl ether carboxylates are lauryl (C₁₂).

SUMMARY OF THE INVENTION

[0006] We have found that particular surfactant mixes with a particular mix of anionic surfactants with a low amount of nonionic surfactant enhance the cleaning benefit of alkyl ether carboxylates.

[0007] In one aspect, the invention provides an aqueous liquid laundry detergent composition comprising:

- (i) from 5 to 25 wt.% of alcohol ether sulfate anionic surfactant and linear alkyl benzene sulfonate anionic surfactant, wherein the weight fraction of alcohol ether sulfate to linear alkyl benzene sulfonate is from 0.6 to 1;
- (ii) from 2 to 6 wt.% of an alkyl ether carboxylic acid anionic surfactant of the following structure:



wherein:

R₂ is selected from C₁₆ to C₁₈ linear alkyl chains, wherein n is selected from 10 to 20, and wherein the weight fraction of alkyl ether carboxylic acid to (linear alkyl benzene sulfonate surfactant + alkyl ether sulfate surfactant) is from 0.1 to 1;

(iii) at least 60 wt.% water;

(iv) up to 4 wt.% of an ethoxylated alcohol non-ionic surfactant, wherein the weight fraction of ethoxylated alcohol non-ionic surfactant to (linear alkyl benzene sulfonate surfactant + alkyl ether sulfate surfactant) is from 0.1 to 0.2; and,

(v) from 0 to 1 wt.% of phosphorous containing chemicals.

[0008] In a second aspect the invention provides 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 laundry detergent composition as defined in the first aspect; and,

b) allowing said aqueous laundry detergent 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.

DETAILED DESCRIPTION OF THE INVENTION

[0009] Weight percentages (wt.%) outlined herein are weight percentage based on the total composition unless otherwise stated.

[0010] 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.

[0011] Preferably the clothes to be washed contain 0.3 to 3 wt.% human sebum.

[0012] In the method aspects of the present invention the surfactant used is preferably as preferred for the composition aspects of the present invention.

[0013] Domestic methods are preferably conducted in a domestic washing machine or by hand washing. The temperature of the wash is preferably from 280 to 320K. The main wash time is preferably 10 to 60 minutes.

[0014] The textile is preferably an item of clothing, bedding or table cloth. Preferred items of clothing are polycotton containing shirts, trousers, underwear and jumpers.

[0015] The composition has a pH of from 7 to 11, preferably from 7 to 10. The pH may suitably be measured whereby a dilution of 5g/L of the aqueous liquid laundry detergent in demineralised water has the stated pH.

[0016] The compositions of the invention may comprise from 0 to 1 wt.% of phosphorous containing chemicals. So the formulation may (and preferably is) free from phosphorous containing chemicals, but when present, they may only be present at a level up to 1 wt.% based on the total formulation.

[0017] The surfactants of invention may be neutralised with any suitable base. Typical amine used to neutralise surfactants are monoethanolamine, triethanolamine, diisopropanolamine, triisopropanolamine, monoamino hexanol, 2-[(2-methoxyethyl) methylamino]- ethanol, propanolamine, N-methylethanolamine, diethanolamine, monobutanol amine, isobutanolamine, monopentanol amine, l-amino-3-(2-methoxyethoxy)-2-propanol, 2-methyl-4-(methylamino)-2-butanol, 6-amino-l-hexanol, heptaminol, isoetarine, norepinephrine, sphingosine, phenylpropanolamine and mixtures thereof.

[0018] The surfactants of invention are preferably neutralized with an aqueous solution of sodium hydroxide.

[0019] It is preferred that the aqueous liquid laundry detergent composition comprises less than or equal to 5 wt.% (i.e. from 0 to 5 wt.%), more preferably less than or equal to 0.2 wt.% (i.e. from 0 to 0.2 wt.%) of hydrotope selected from: ethylene glycol; 1,3 propanediol; 1,2 propanediol; tetramethylene glycol; pentamethylene glycol; hexamethylene glycol; 2,3-butane diol; 1,3 butanediol; diethylene glycol; triethylene glycol; polyethylene glycol; glycerol formal dipropylene glycol; polypropylene glycol; dipropylene glycol n-butyl ether; and, mixtures thereof. Preferably the hydrotope at the low level is selected from the group comprising: 1,2 propanediol; dipropylene glycol; polypropylene glycol; 2,3-butane diol; dipropylene glycol n-butyl ether; and, mixtures thereof.

[0020] The detergent is preferably blue, green or violet in colour. The detergent is preferably transparent with a maximum optical density (1cm) of 1.5 in the range 400 to 700nm. Weights of anionic surfactants are calculated as their protonated form.

Alkyl Ether Carboxylic Acid

[0021] The liquid laundry composition comprises from 2 to 6 wt.%, of the alkyl ether carboxylic acid anionic surfactant.

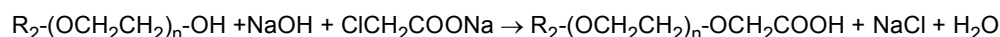
[0022] Weights of alkyl ether carboxylic acid are calculated as the protonated form, $R_2-(OCH_2CH_2)_n-OCH_2COOH$. They may be used as salt version for example sodium salt, or amine salt. The alkyl chain (R_2) is selected from C_{16} to C_{18} linear alkyl chains.

[0023] The alkyl ether carboxylic acid has n selected from 10 to 20.

[0024] The weight fraction of alkyl ether carboxylic acid to (linear alkyl benzene sulfonate surfactant + alkyl ether sulfate surfactant) is from 0.1 to 1, preferably from 0.1 to 0.6, more preferably from 0.2 to 0.5.

[0025] Alkyl ether carboxylic acid are available from Kao (Akypo®), Huntsman (Empicol®) and Clariant (Emulsogen®). The sodium salt of the alkyl ether carboxylate is most preferred. Alkyl ether carboxylic acids synthesis is discussed in Anionic Surfactants Organic Chemistry edited by H.W. Stache (Marcel Dekker, New York 1996).

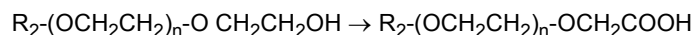
[0026] They may be synthesised via the reaction of the corresponding alcohol ethoxylate with chloroacetic acid or monochloro sodium acetate in the presence of NaOH:-



[0027] 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.

[0028] NaCl from the synthesis may be present in the aqueous liquid laundry detergent composition. Additional NaCl may be added to the composition.

[0029] They alkyl ether carboxylic acid may also be synthesised via an oxidation reaction:-



[0030] 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.

Alcohol Ether Sulphate

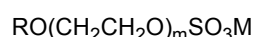
[0031] The composition comprises from 5 to 25 wt. % of alcohol ether sulfate anionic surfactant and linear alkyl benzene sulfonate anionic surfactant, wherein the weight fraction of alcohol ether sulfate to linear alkyl benzene sulfonate is from 0.6 to 1.

[0032] The weight levels of 5 to 25 wt. % relate to the total amount of alcohol ether sulfate anionic surfactant + linear alkyl benzene sulfonate anionic surfactant.

[0033] The weight fraction indicates that the alcohol ether sulfate anionic surfactant is present at a weight level of up from 60 wt. % to 100 wt. % of the weight level of the linear alkyl benzene sulfonate surfactant. That is, the alcohol ether sulfate anionic surfactant is always present at a level no greater than the linear alkyl benzene sulfonate anionic surfactant.

[0034] Alkyl ether sulphate synthesis is discussed in Anionic Surfactants Organic Chemistry edited by H.W. Stache (Marcel Dekker, New York 1996). Alcohol ether sulphates are produced by the sulphonation of the corresponding alcohol ethoxylate.

[0035] The preferred alkyl ether sulphate surfactants hereof are of the formula:



wherein R is an unsubstituted C_{10} - C_{18} linear alkyl chain, more preferably C_{12} - C_{15} alkyl chain, most preferably lauryl; m is from 0.5 to 6, more preferably from 0.5 to 3, most preferably from 2.5 to 3.5; and M is a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Weights are expressed as the protonated form.

Linear Alkyl Benzene Sulfonate

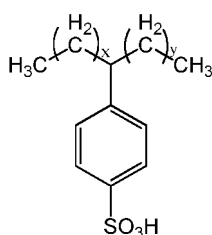
[0036] The composition comprises from 5 to 25 wt. % of alcohol ether sulfate anionic surfactant and linear alkyl benzene sulfonate anionic surfactant, wherein the weight fraction of alcohol ether sulfate to linear alkyl benzene sulfonate is from 0.6 to 1.

[0037] The weight levels of 5 to 25 wt. % relate to the total amount of alcohol ether sulfate anionic surfactant + linear alkyl benzene sulfonate anionic surfactant.

[0038] The weight fraction indicates that the alcohol ether sulfate anionic surfactant is present at a weight level of up from 60 wt. % to 100 wt. % of the weight level of the linear alkyl benzene sulfonate surfactant. That is, the alcohol ether sulfate anionic surfactant is always present at a level no greater than the linear alkyl benzene sulfonate anionic surfactant.

[0039] Linear alkyl benzene sulfonate is the neutralised form of linear alkyl benzene sulfonic acid. Neutralisation may be carried out with any suitable base. The sodium salt is most preferred.

[0040] Linear alkyl benzene sulfonic acid has the structure:



[0041] Preferably where $x + y = 7, 8, 9$ or 10 .

[0042] Preferably $x + y = 8$ is present at a weight level greater than 28 wt. % of the total level of the linear alkyl benzene anionic surfactant.

[0043] Preferably $x + y = 9$ is present at greater than 28 wt. % of the total level of the linear alkyl benzene anionic surfactant. Weights are expressed as the protonated form.

[0044] The surfactant may be produced by a variety of different routes. Synthesis is discussed in Anionic Surfactants Organic Chemistry edited by H.W. Stache (Marcel Dekker, New York 1996).

[0045] Linear alkyl benzene sulfonic acid may be made by the sulfonation of linear alkyl benzene. The sulfation can be carried out with concentrated sulphuric acid, oleum or sulphur trioxide. Linear alkyl benzene sulfonic acid produced by reaction of linear alkyl benzene with sulphur trioxide is preferred.

[0046] Linear alkyl benzene may be produced by a variety of routes. Examples include: Benzene may be alkylated with n-alkenes using HF catalyst.

[0047] Benzene may be alkylated with n-alkenes in a fixed bed reactor with a solid acidic catalyst such as Alumosilicate (DETAL process).

[0048] Benzene may be alkylated with n-alkenes using an aluminium chloride catalyst. Benzene may be alkylated with n-chloroparaffins using an aluminium chloride catalyst.

Water

[0049] The liquid detergent composition is aqueous. It comprises at least 60 wt.% water. Preferably it comprises at least 65 wt.%, more preferably at least 70 wt.%, most preferably at least 75 wt.% water. Exemplar preferred weight ranges of water levels include from 60 to 94.5 wt.%, preferably from 62.5 to 92.5 wt.%, more preferably from 65 to 90 wt.%.

Ethoxylated alcohol non-ionic surfactant

[0050] Ethoxylated alcohol non-ionic surfactant is present at a maximum level 4 wt.%.

[0051] The weight fraction of ethoxylated alcohol non-ionic surfactant to (linear alkyl benzene sulfonate surfactant + alkyl ether sulfate surfactant) is from 0.1 to 0.2, preferably from 0.1.

[0052] This means that the ethoxylated alcohol non-ionic surfactant is present at a weight level of up to a fifth (preferably a tenth) of the weight level of the (linear alkyl benzene sulfonate surfactant + alkyl ether sulfate surfactant).

[0053] The non-ionic surfactant is preferably fatty alcohol ethoxylate non-ionic surfactant.

[0054] The ethoxylated nonionic surfactant is preferably a primary alcohol ethoxylate, more preferably C₈ to C₂₀ aliphatic alcohols ethoxylated with an average of from 1 to 20 moles of ethylene oxide per mole of alcohol. Most preferably the ethoxylated alcohol non-ionic surfactant is selected from a C₁₂ to C₁₅ primary aliphatic alcohol with 7 to 9 moles of ethylene oxide per mole of alcohol; R₂-(OCH₂CH₂)_n-OH and R₂-(OCH₂CH₂)_{n+1}-OH.

[0055] Preferably the alkyl chain is linear.

Further Surfactant

[0056] The aqueous liquid laundry detergent may comprises further surfactants, for example those described in "Surface Active Agents" Vol. 1, by Schwartz & Perry, Interscience 1949, Vol. 2 by Schwartz, Perry & Berch, Interscience 1958, in the current edition of "McCutcheon's Emulsifiers and Detergents" published by Manufacturing Confectioners Company or in "Tenside Taschenbuch", H. Stache, 2nd Edn., Carl Hauser Verlag, 1981 or in Anionic Surfactants: Organic Chemistry edited by Helmut W. Stache (Marcel Dekker 1996).

[0057] Examples of suitable further anionic detergent compounds are; alkyl sulphates, especially those obtained by sulphating linear or branched C₈ to C₁₈ alcohols; soaps; alkyl (preferably methyl) ester sulfonates, and mixtures thereof.

The further surfactant is preferably anionic. Preferably the weight fraction of further surfactant to (linear alkyl benzene sulfonate surfactant + alkyl ether sulfate surfactant) is from 0 to 0.2. This means that the further surfactant may be absent (so the weight fraction of further surfactant to [linear alkyl benzene sulfonate surfactant + alkyl ether sulfate surfactant] is 0); or if the further surfactant is present, then it is present at a weight level of up to a 20% of the weight level of the (linear alkyl benzene sulfonate surfactant + alkyl ether sulfate surfactant).

[0058] Preferably the weight fraction of further surfactant to (linear alkyl benzene sulfonate surfactant + alkyl ether sulfate surfactant) is from 0 to 0.2, more preferably from 0 to 0.1. Exemplar preferable weight fractions of further surfactant (when present) to (linear alkyl benzene sulfonate surfactant + alkyl ether sulfate surfactant) include 0.01 to 0.2, more preferably from 0.01 to 0.1.

[0059] The further surfactant is preferably an anionic surfactant.

[0060] So preferably the weight fraction of further surfactant (linear alkyl benzene sulfonate surfactant + alkyl ether sulfate surfactant) is from 0 to 0.2, more preferably from 0 to 0.1. Exemplar preferable weight fractions of further surfactant (when present) to (linear alkyl benzene sulfonate surfactant + alkyl ether sulfate surfactant) include 0.01 to 0.2, more preferably from 0.01 to 0.1.

[0061] Preferably any further surfactant is present at a level of from 0 to 4 wt.%.

Alkoxyate Polyethylene Imine

[0062] The alkoxyated polyethylene imine comprises a polyethyleneimine backbone wherein the modification of the polyethyleneimine backbone is intended to leave the polymer without quaternisation. Such materials may be represented as PEI(X)YAO where X represents the molecular weight of the unmodified PEI and Y represents the average moles of alkoxylation (AO) per available NH in the unsubstituted polyethyleneimine backbone. Y is preferably from 7 to 40 more preferably it is in the range of 16 to 26, most preferably 18 to 22. X is selected to be from about 300 to about 10000 weight average molecular weight and is preferably about 600.

[0063] The alkoxylation is preferably selected from ethoxylation or propoxylation, or a combination of the two, Ethoxylation is most preferred. The alkoxy chains may be capped with groups selected from: H; CH₃; SO₃⁻; CH₂COO⁻; PO₃²⁻; C₂H₅; n-propyl, i-propyl; n-butyl; t-butyl; and, sulfosuccinate, most preferably H.

[0064] Most preferably the alkoxyated PEI is PEI(600)20EO.

[0065] Inclusion levels of the alkoxyated polyethylenimine may be from 0.1 to 10 wt.%.

Terephthalate Polyester Soil Release Polymer

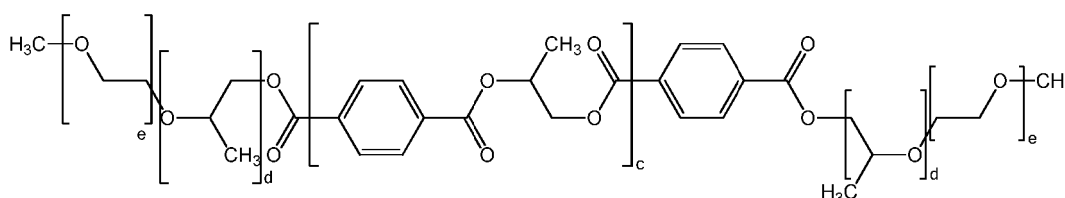
[0066] Terephthalate Polyester Soil Release Polymer comprise polymers of aromatic dicarboxylic acids and alkylene glycols (including polymers containing polyalkylene glycols), as described in WO2009/153184, EP2692842 and WO2014/019903.

[0067] Examples of Terephthalate Polyester Soil Release Polymer are the REPEL-O-TEX® line of polymers supplied by Rhodia, including REPEL-O-TEX® SRP6 and REPEL-O-TEX® SF-2. Other suitable soil release polymers include TexCare® polymers, including TexCare® SRA-100, TexCare® SRA-300, TexCare® SRN-100, TexCare® SRN-170, TexCare® SRN-240, TexCare® SRN-300, and TexCare® SRN-325, all supplied by Clariant.

[0068] Preferred structure are $-(Z)_a-O-OC-Ar-CO-)_b$ and $(Z)_a-O-OC-[Ar-CO-O-C_3H_6-O-OC]_b-Ar-CO-O-(Z)_a$, where Ar is selected from 1,4 substituted phenylene and 1,3 substituted phenylene substituted in the 5 position with a sulphonates (SO₃⁻) group; Z is selected from ethoxy;propoxy; and mixtures of ethoxy and propoxy; a is from 5 to 100 and b from 2 to 40. C₃H₆ is i-propyl.

[0069] The alkoxy chains are capped with groups selected from H; CH₃; SO₃⁻; CH₂COO⁻; PO₃²⁻; C₂H₅; n-propyl, i-propyl; n-butyl; t-butyl; and, sulfosuccinate.

[0070] Most preferably the terephthalate polyester soil release polymer is:



wherein c is from 4 to 9; d is from 1 to 3; e is from 40 to 50.

[0071] The terephthalate polyester soil release polymer may be present at levels from 0.1 to 8 wt.%.

[0072] In one embodiment, preferably the aqueous liquid laundry detergent composition does not comprise from 0.1 to 3 wt.% terephthalate polyester soil release polymer.

Polymers

[0073] The composition may comprise one or more further polymers.

[0074] Examples are carboxymethylcellulose, poly (ethylene glycol), poly(vinyl alcohol), polycarboxylates such as polyacrylates, maleic/acrylic acid copolymers and methacrylate/acrylic acid copolymers. Co-polymers as described in WO2014/082955 (Unilever) may be present.

[0075] Polymers present to prevent dye deposition may be present, for example poly(vinylpyrrolidone), poly(vinylpyridine-N-oxide), and poly(vinylimidazole).

Such polymers are preferably present at levels of less than 0.5 wt.%.

[0076] The composition is preferably devoid of silicone polymers and polymers bearing quaternised N groups.

[0077] Where the polymer is considered a builder and/or sequestrant, then the level of polymer is included in the total level of builder and sequestrants.

Builders and Sequestrants

[0078] The detergent compositions may also optionally contain relatively low levels of organic detergent builder or sequestrant material. Examples include the alkali metal, citrates, succinates, malonates, carboxymethyl succinates, carboxylates, polycarboxylates and polyacetyl carboxylates. Specific examples include sodium, potassium and lithium salts of oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, ethylene diamine tetra-acetic acid, diethylene-triamine-pentaacetic acid, alkyl- or alkenylsuccinic acid, nitrilotriacetic acid, and citric acid.

[0079] If utilized, the aqueous liquid laundry detergent formulation comprise from 0.1% to 3.0 wt.% builder and sequestrant material. Citrate is most preferred.

Phosphorous containing chemical

[0080] Phosphorous containing chemicals are inorganic or organic chemicals that contain phosphorous.

[0081] Examples are sodium triphosphosphate, DEQUEST™, organic phosphonate type sequestering agents sold by Monsanto and alkanehydroxy phosphonates.

[0082] The aqueous liquid laundry detergent composition comprises from 0 to 1 wt.% of phosphorous containing chemicals.

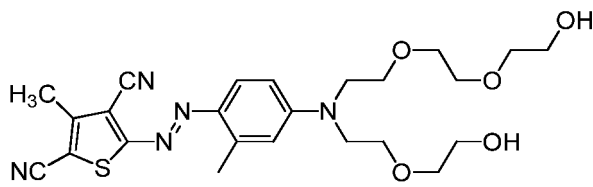
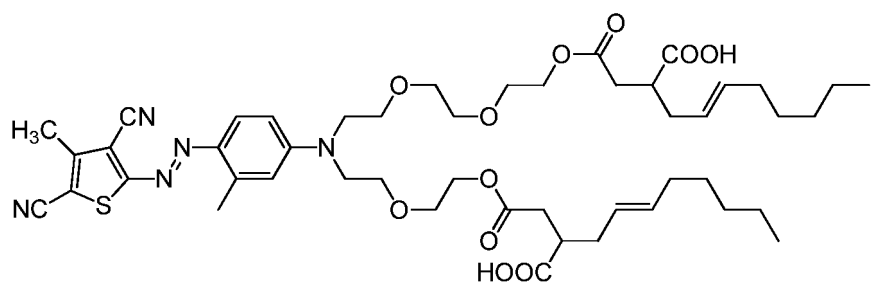
Shading Dye

[0083] Dyes are described in Color Chemistry Synthesis, Properties and Applications of Organic Dyes and Pigments, (H Zollinger, Wiley VCH, Zurich, 2003) and, Industrial Dyes Chemistry, Properties Applications. (K Hunger (ed), Wiley-VCH Weinheim 2003).

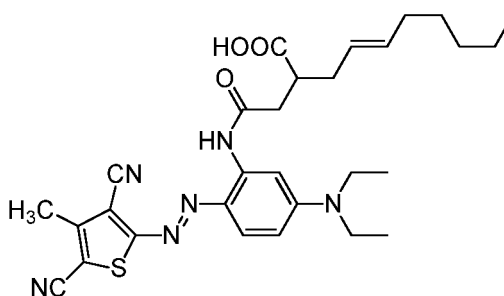
[0084] Shading Dyes for use in laundry detergents preferably have an extinction coefficient at the maximum absorption in the visible range (400 to 700nm) of greater than 5000 L mol⁻¹ cm⁻¹, preferably greater than 10000 L mol⁻¹ cm⁻¹. The dyes are blue or violet in colour.

[0085] Preferred shading dye chromophores are azo, azine, and anthraquinone.

[0086] Preferred examples of azo dyes are Direct Violet 9, Direct Violet 99, Direct Violet 35 and the dyes shown below:



and,



[0087] Azine dye are preferably selected from sulphonated phenazine dyes. Preferred examples are acid blue 98, acid violet 50, dye with CAS-No 72749-80-5, acid blue 59.

[0088] Preferred Anthraquinone dyes are Disperse Violet 28, and 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 isopropyl alcohol groups by propoxylation. Preferably the polyethylene imine before reaction with the dye and the propoxylation has a molecular weight of 600 to 1800.

[0089] A mixture of shading dyes may be used.

[0090] The shading dye is preferably present in the composition in range from 0.0001 to 0.5 wt.%, more 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 class and particular efficacy within any particular class.

Enzymes

[0091] Preferably the level of each enzyme in the laundry composition of the invention is from 0.0001 wt.% to 0.1 wt.% protein.

[0092] A protease enzyme is preferably present in the aqueous liquid laundry detergent composition. Protease enzymes hydrolyse bonds within peptides and proteins, in the laundry context this leads to enhanced removal of protein or peptide containing stain

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

[0093] A lipase enzyme is preferably present in the aqueous liquid laundry detergent composition. Preferred commercially available lipase enzymes include Lipolase™ and Lipolase Ultra™, Lipex™ and Lipoclean™ (Novozymes A/S).

[0094] 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, described in more detail in GB 1,296,839, or the *Bacillus* sp. strains disclosed in WO 95/026397 or WO 00/060060. Commercially available amylases are Duramyl™, Termamyl™, Termamyl Ultra™, Natalase™, Stainzyme™, Fungamyl™ and BAN™ (Novozymes A/S), Rapidase™ and Purastar™ (from Genencor International Inc.).

Fluorescent Agent

[0095] 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.

[0096] Preferred classes of fluorescer 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 Blankophor (Trade Mark) HRH, and Pyrazoline compounds, e.g. Blankophor SN.

[0097] Preferred fluorescers 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.

[0098] The total amount of the fluorescent agent or agents used in the composition is preferably from 0.0001 to 0.5 wt.%, more preferably 0.005 to 2 wt.%, most preferably 0.05 to 0.25 wt.%.

Perfume

[0099] The composition preferably comprises a perfume.

[0100] The perfume is preferably included in the range from 0.01 to 2 wt.%, more preferably 0.05 to 0.5 wt.%, most preferably from 0.1 to 1 wt.%. 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 80th Annual Edition, published by Schnell Publishing Co.

[0101] The International Fragrance Association has published a list of fragrance ingredients (perfumes) in 2011: (<http://www.ifraorg.org/en-us/inredients#.U7Z4hPldWzk>).

[0102] The Research Institute for Fragrance Materials provides a database of perfumes (fragrances) with safety information.

[0103] 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.

[0104] It is preferred that the laundry treatment composition does not contain a peroxygen bleach, e.g., sodium percarbonate, sodium perborate, and peracid.

[0105] The liquid laundry detergent composition may be present in a water-soluble unit dose article. In such an embodiment, the water-soluble unit dose article comprises at least one water-soluble film shaped such that the unit-dose article comprises at least one internal compartment surrounded by the water-soluble film. The at least one compartment comprises the liquid laundry detergent composition. The water-soluble film is sealed such that the liquid laundry detergent

composition does not leak out of the compartment during storage. However, upon addition of the water-soluble unit dose article to water, the water-soluble film dissolves and releases the contents of the internal compartment into the wash liquor.

Experimental

[0106] An aqueous liquid laundry detergent was prepared of the following formulation:

Ingredient	Wt. %
Mono propylene glycol	2.2
Triethanoamine	1.5
Surfactants other than AEC	11.6
Citric acid	2.0
CaCl ₂ dihydrate	0.2
NaCl	0.2
Tinopal CBS-X (fluorescer BASF)	0.3
Sodium Hydroxide	To pH=8.4
Alkyl Ether Carboxylate (AEC)	See text
Water	balance

[0107] The surfactants other than AEC were linear alkyl benzene sulfonate (LAS), sodium lauryl ether sulfate (SLES) with 3 moles of ethoxylation, and a non-ionic (NI) a C₁₂-C₁₅ linear alcohol alcohol with 7 moles of ethoxylation. The ratios of the 3 are given in the results table below. Formulations were made with and without the addition of 4 wt.% of Alkyl Ether Carboxylate (AEC). The AEC used had 10 moles of ethoxylation and an oleyl alkyl chain.

[0108] The formulation was used to wash eight 5 x 5cm EMPA 117 stain monitor (blood/milk/ink stain on polycotton) in a tergotometer set at 200rpm. A 60 minute wash was conducted in 800ml of 26° French Hard water at room temperature (293K), with 2.3g/L of the formulation. To simulate oily soil (7.5 g) of an SBL2004 soil strip (ex Warwick Equest) cut into 4 equal pieces was added to the wash liquor.

[0109] Once the wash had been completed the cotton monitors were rinsed once in 400ml clean water, removed, dried and the colour measured on a reflectometer and expressed as the R460, which is the % reflectance at 460nm (UV excluded).

[0110] The bigger the delta in the R460 value, the cleaner the fabric is compared to the control.

[0111] From this the $\Delta R460$ value was calculated:

$$\Delta R460 = L(AEC) - L(\text{control})$$

[0112] The larger the $\Delta R460$ value the greater the increase in performance of the formulation by introduction of the Alkyl Ether Carboxylate (AEC). 95% confidence limits based on the 8 separate EMPA 117 pieces were calculated.

[0113] The results are shown below:

	LAS	NI	SLES	$\Delta R460$	95%
<i>Comparative A</i>	40	10	50	4.2	0.5
<i>Comparative B</i>	38	25	38	4.4	0.3
<i>1</i>	50	0	50	9.5	0.7
<i>Inventive 2</i>	45	10	45	8.3	0.4

[0114] The comparative example A is considered to fairly reflect the disclosure of the prior art WO 2016/180552 (example 1) and DE 10 2013 218 614A (example B) which disclose exemplar formulations having LAS:NI:SLES in weight ratios of 4:1:5 (WO 2016/180552) and 4:2:5 (DE 10 2013 218 614A).

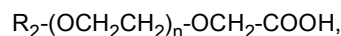
[0115] The inventive formulation which included alcohol ether sulfate anionic surfactant and linear alkyl benzene

sulfonate anionic surfactant in a certain weight fraction, along with a maximum low amount of nonionic surfactant showed a much greater benefit from the addition of the AEC.

Claims

1. An aqueous liquid laundry detergent composition having a pH of from 7 to 11 comprising:

- (i) from 5 to 25 wt.% of alcohol ether sulfate anionic surfactant and linear alkyl benzene sulfonate anionic surfactant, wherein the weight fraction of alcohol ether sulfate to linear alkyl benzene sulfonate is from 0.6 to 1;
- (ii) from 2 to 6 wt.% of an alkyl ether carboxylic acid anionic surfactant of the following structure:



wherein:

R₂ is selected from C₁₆ to C₁₈ linear alkyl chains, wherein n is selected from 10 to 20, and wherein the weight fraction of alkyl ether carboxylic acid to (linear alkyl benzene sulfonate surfactant + alkyl ether sulfate surfactant) is from 0.1 to 1;

(iii) at least 60 wt.% water;

(iv) up to 4 wt.% of an ethoxylated alcohol non-ionic surfactant, wherein the weight fraction of ethoxylated alcohol non-ionic surfactant to (linear alkyl benzene sulfonate surfactant + alkyl ether sulfate surfactant) is from 0.1 to 0.2; and,

(v) from 0 to 1 wt.% of phosphorous containing chemicals.

2. An aqueous liquid laundry detergent composition according claim 1, wherein the composition optionally comprises a further anionic surfactant, wherein the weight fraction of further anionic surfactant to (linear alkyl benzene sulfonate surfactant + alkyl ether sulfate surfactant) is from 0 to 0.2, preferably 0 to 0.1, more preferably 0.01 to 0.2, most preferably from 0.01 to 0.1.

3. An aqueous liquid laundry detergent composition according to any one of the preceding claims, wherein the weight fraction of alkyl ether carboxylic acid to (linear alkyl benzene sulfonate surfactant + alkyl ether sulfate surfactant) is from 0.1 to 0.6, preferably 0.2 to 0.5.

4. An aqueous liquid laundry detergent composition according to any one of the preceding claims, wherein the alkyl ether sulfate is lauryl ether sulfate anionic surfactant and has a mole average of from 2.5 to 3.5 of ethoxylation.

5. An aqueous liquid laundry detergent composition according to any one of the preceding claims, having a pH of from 7 to 10.

6. A domestic method of treating a textile, the method comprising the steps of:

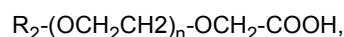
a) treating a textile with from 1 g/L of an aqueous solution of the laundry detergent composition as defined in any one of the preceding claims; and,

b) allowing said aqueous laundry detergent 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.

Patentansprüche

1. Wässrige flüssige Waschmittelzusammensetzung mit einem pH von 7 bis 11, umfassend:

- (i) 5 bis 25 Gew.-% anionisches Alkoholethersulfat-Tensid und anionisches lineares Alkylbenzolsulfonat-Tensid, wobei der Gewichtsanteil von Alkoholethersulfat zu linearem Alkylbenzolsulfonat 0,6 bis 1 beträgt;
- (ii) 2 bis 6 Gew.-% eines anionischen Alkylethercarbonsäure-Tensids der folgenden Struktur:



worin:

R_2 ausgewählt ist aus linearen C_{16} - bis C_{18} -Alkylketten, worin n ausgewählt ist aus 10 bis 20 und worin der Gewichtsanteil von Alkylethercarbonsäure zu (linearem Alkylbenzolsulfonat-Tensid + Alkylethersulfat-Tensid) 0,1 bis 1 beträgt;

(iii) mindestens 60 Gew.-% Wasser;

(iv) bis zu 4 Gew.-% eines nichtionischen ethoxylierten Alkohol-Tensids, wobei der Gewichtsanteil des nichtionischen ethoxylierten Alkohol-Tensids zu (linearem Alkylbenzolsulfonat-Tensid + Alkylethersulfat-Tensid) 0,1 bis 0,2 beträgt; und

(v) 0 bis 1 Gew.-% Phosphor enthaltende Chemikalien.

2. Wässrige flüssige Waschmittelzusammensetzung nach Anspruch 1, wobei die Zusammensetzung gegebenenfalls ein weiteres anionisches Tensid umfasst, wobei der Gewichtsanteil des weiteren anionischen Tensids zu (linearem Alkylbenzolsulfonat-Tensid + Alkylethersulfat-Tensid) 0 bis 0,2, bevorzugt 0 bis 0,1, bevorzugter 0,01 bis 0,2, am meisten bevorzugt von 0,01 bis 0,1, beträgt.

3. Wässrige flüssige Waschmittelzusammensetzung nach irgendeinem der vorhergehenden Ansprüche, wobei der Gewichtsanteil von Alkylethercarbonsäure zu (linearem Alkylbenzolsulfonat-Tensid + Alkylethersulfat-Tensid) 0,1 bis 0,6, bevorzugt 0,2 bis 0,5, beträgt.

4. Wässrige flüssige Waschmittelzusammensetzung nach irgendeinem der vorhergehenden Ansprüche, wobei das Alkylethersulfatanionische Laurylethersulfat-Tensid ist und ein molares Mittel von 2,5 bis 3,5 der Ethoxylierung aufweist.

5. Wässrige flüssige Waschmittelzusammensetzung nach irgendeinem der vorhergehenden Ansprüche mit einem pH von 7 bis 10.

6. Verfahren im Haushalt zur Behandlung eines Textils, wobei das Verfahren die folgenden Schritte umfasst:

a) Behandeln eines Textils mit ab 1 g/L einer wässrigen Lösung der Waschmittelzusammensetzung wie in irgendeinem der vorhergehenden Ansprüche definiert; und

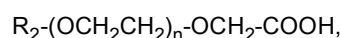
b) man die wässrige Waschmittellösung für einen Zeitraum von 10 Minuten bis 2 Tagen mit dem Textil in Kontakt bleiben lässt, dann Spülen und Trocknen des Textils.

Revendications

1. Composition de détergent de lessive liquide aqueuse ayant un pH de 7 à 11 comprenant :

(i) de 5 à 25 % en masse de tensioactif anionique d'éthersulfate d'alcool et un tensioactif anionique de benzènesulfonate d'alkyle linéaire, dans laquelle la fraction massique d'éthersulfate d'alcool à benzènesulfonate d'alkyle linéaire est de 0,6 à 1 ;

(ii) de 2 à 6 % en masse d'un tensioactif anionique d'acide alkyléther carboxylique de la structure suivante :



dans laquelle :

R_2 est choisi parmi des chaînes alkyle linéaires en C_{16} à C_{18} , dans laquelle n est choisi de 10 à 20, et dans laquelle la fraction massique d'acide alkyléther carboxylique à (tensioactif de benzènesulfonate d'alkyle linéaire + tensioactif d'éthersulfate d'alkyle) est de 0,1 à 1 ;

(iii) au moins 60 % en masse d'eau ;

(iv) jusqu'à 4 % en masse d'un tensioactif non-ionique d'alcool éthoxylé, dans laquelle la fraction massique de tensioactif non ionique d'alcool éthoxylé à (tensioactif de benzènesulfonate d'alkyle linéaire + tensioactif d'éthersulfate d'alkyle) est de 0,1 à 0,2; et,

(v) de 0 à 1 % en masse de produits chimiques contenant du phosphore.

2. Composition de détergent de lessive liquide aqueuse selon la revendication 1, dans laquelle la composition comprend éventuellement un autre tensioactif anionique, dans laquelle la fraction massique de l'autre tensioactif anionique à (tensioactif de benzènesulfonate d'alkyle linéaire + tensioactif d'éthersulfate d'alkyle) est de 0 à 0,2, de préférence de 0 à 0,1, encore mieux de 0,01 à 0,2, bien mieux encore de 0,01 à 0,1.

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3. Composition de détergent de lessive liquide aqueuse selon l'une quelconque des revendications précédentes, dans laquelle la fraction massique d'acide alkyléther carboxylique à (tensioactif de benzènesulfonate d'alkyle linéaire + tensioactif d'éthersulfate d'alkyle) est de 0,1 à 0,6, de préférence de 0,2 à 0,5.

5 4. Composition de détergent de lessive liquide aqueuse selon l'une quelconque des revendications précédentes, dans laquelle l'éthersulfate d'alkyle est un tensioactif anionique d'éthersulfate de lauryle et présente une moyenne en mole de 2,5 à 3,5 d'éthoxylation.

10 5. Composition de détergent de lessive liquide aqueuse selon l'une quelconque des revendications précédentes, ayant un pH de 7 à 10.

6. Procédé domestique de traitement d'un textile, le procédé comprenant les étapes de :

15 a) traitement d'un textile avec 1 g/l d'une solution aqueuse de la composition de détergent de lessive selon l'une quelconque des revendications précédentes ; et,
b) laisser ladite solution de détergent de lessive aqueuse rester en contact avec le textile sur une période de 10 minutes à 2 jours, puis rinçage et séchage du textile.

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- WO 2016180552 A [0003] [0114]
- DE 102013218614 [0004]
- WO 2017054983 A [0005]
- DE 3135946 [0030]
- DE 2816127 [0030]
- EP 0304763 A [0030]
- WO 2009153184 A [0066]
- EP 2692842 A [0066]
- WO 2014019903 A [0066]
- WO 2014082955 A [0074]
- GB 1296839 A [0094]
- WO 95026397 A [0094]
- WO 00060060 A [0094]
- DE 102013218614 A [0114]

Non-patent literature cited in the description

- Anionic Surfactants Organic Chemistry. Marcel Dekker, 1996 [0044]
- **SCHWARTZ ; PERRY**. Surface Active Agents. Interscience, 1949, vol. 1 [0056]
- **SCHWARTZ ; PERRY ; BERCH**. SURFACE ACTIVE AGENTS. Interscience, 1958, vol. 2 [0056]
- McCutcheon's Emulsifiers and Detergents. Manufacturing Confectioners Company [0056]
- **H. STACHE**. Tenside Taschenbuch. Carl Hauser Verlag, 1981 [0056]
- Anionic Surfactants: Organic Chemistry. Marcel Dekker, 1996 [0056]
- **H ZOLLINGER**. Color Chemistry Synthesis, Properties and Applications of Organic Dyes and Pigments. Wiley VCH, 2003 [0083]
- Industrial Dyes Chemistry, Properties Applications. Wiley-VCH, 2003 [0083]
- International Buyers Guide. CFTA Publications, 1992 [0100]
- Chemicals Buyers Directory. Schnell Publishing Co, 1993 [0100]
- a list of fragrance ingredients (perfumes). *The International Fragrance Association*, 2011 [0101]