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(54) **DETERGENT COMPOSITIONS**

(57) The invention provides a detergent composition for the non-oxidative laundering of fabric stains, the composition comprising:

(a) from 0.1 to 10% (by weight based on the total weight of the composition) of (1,6-dihydroxy-1,6,6-triphosphohexyl) phosphonic acid and/or a salt thereof; and

(b) from 3 to 80% (by weight based on the total weight of the composition) of one or more deterative surfactants.

The invention also provides a method for the non-oxidative laundering of fabric stains, comprising diluting a dose of the detergent composition defined above to obtain a wash liquor, and washing the stained fabric with the wash liquor so formed.

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DescriptionField of the Invention

5 **[0001]** The present invention relates to detergent compositions for the non-oxidative laundering of fabric stains.

Background and Prior Art

10 **[0002]** Significant efforts have been invested in recent years towards improving the washing performance of laundry detergents at low temperatures. Lifecycle studies show that the largest environmental impact of the laundry process is during the use phase, especially when the water of the main wash is heated. Consequently, a temperature reduction is a pivotal driver to improve the overall sustainability profile of the laundry process. Washing at cooler temperatures is also advisable for care of coloured and/or delicate fabrics.

15 **[0003]** At the same time, environmental regulations are becoming more stringent in many countries, making it necessary for formulators to produce detergents that reduce potential negative impacts on wastewater and water ways, and reduce greenhouse gas emissions.

20 **[0004]** As consumers move to lower wash temperatures and seek products with improved environmental credentials, the satisfactory removal of stains presents a continuing challenge. Stains are usually caused by molecules of coloured substances deposited on or in fibres or in residual soil. Highly coloured stains are particularly difficult to remove. They often originate from polyphenolic compounds, such as the natural flavonoids found in tea and red wine.

[0005] Oxidizing bleaches such as peroxygen compounds have been used for the oxidative degradation and decolorisation of highly coloured stains. However, peroxygen compounds have reduced efficacy at lower temperatures and cannot generally be incorporated into liquid laundry detergents without storage stability problems. Oxidizing bleaches may also be unsuitable for prolonged or intensive use on coloured or delicate fabrics.

25 **[0006]** Transition metal sequestrants have been used to improve stain removal at low temperatures. However, the most effective of these tend to be phosphorus-based compounds. It would be desirable to improve the weight efficiency of such materials.

[0007] It is an object of the present invention to solve one or more of the above problems.

30 Summary of the Invention

[0008] The present invention provides a detergent composition for the non-oxidative laundering of fabric stains, the composition comprising:

35 (a) from 0.1 to 10% (by weight based on the total weight of the composition) of (1,6-dihydroxy-1,6,6-triphosphonohexyl) phosphonic acid and/or a salt thereof; and

(b) from 3 to 80% (by weight based on the total weight of the composition) of one or more deterative surfactants.

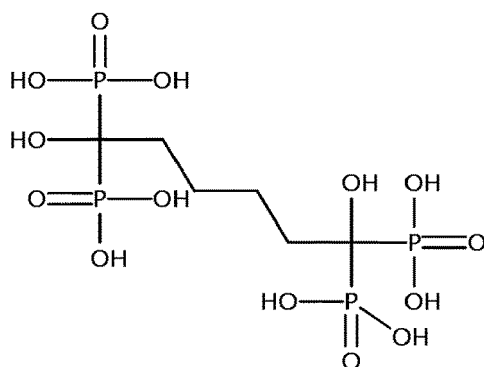
40 **[0009]** The invention also provides a method for the non-oxidative laundering of fabric stains, comprising diluting a dose of the detergent composition defined above to obtain a wash liquor, and washing the stained fabric with the wash liquor so formed.

Detailed Description and Preferred Embodiments

45 **[0010]** (1,6-dihydroxy-1,6,6-triphosphonohexyl) phosphonic acid may be represented by the following formula (I):

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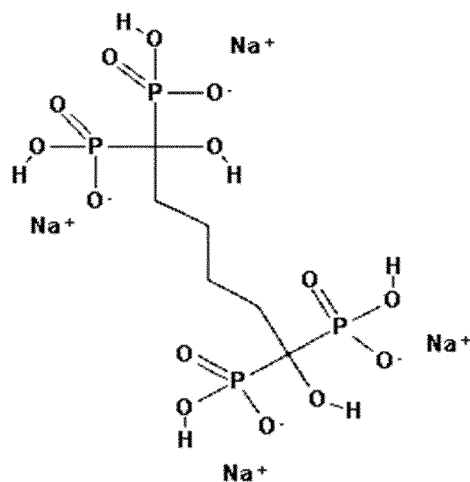
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(I)

[0011] Suitable salts for use in the invention include are those where one or more of the acidic hydrogen atoms in the molecule are replaced by an alkali metal cation such as sodium or potassium, or an ammoniacal counterion such as ammonium, monoethanolamine, (MEA) diethanolamine (DEA) or triethanolamine (TEA).

[0012] Preferred salts are those where one or more of the acidic hydrogen atoms in the molecule are replaced by sodium, such as the tetrasodium salt, which may be represented by the following formula (II):



(II)

[0013] Mixtures of any of the above described materials may also be used.

[0014] The total amount of (1,6-dihydroxy-1,6,6-triphosphonohexyl) phosphonic acid and/or salt thereof in a composition of the invention preferably ranges from about 0.25 to 7.5%, more preferably from 0.5 to 6%, most preferably from 1 to 5% (by weight based on the total weight of the composition).

Detergent Compositions

[0015] The term "detergent composition" in the context of this invention denotes formulated compositions intended for and capable of wetting and cleaning domestic laundry such as clothing, linens and other household textiles. The term "linen" is often used to describe certain types of laundry items including bed sheets, pillow cases, towels, tablecloths, table napkins and uniforms. Textiles can include woven fabrics, non-woven fabrics, and knitted fabrics; and can include natural or synthetic fibres such as silk fibres, linen fibres, cotton fibres, polyester fibres, polyamide fibres such as nylon, acrylic fibres, acetate fibres, and blends thereof including cotton and polyester blends.

[0016] Examples of detergent compositions include heavy-duty detergents for use in the wash cycle of automatic washing machines, as well as fine wash and colour care detergents such as those suitable for washing delicate garments (e.g. those made of silk or wool) either by hand or in the wash cycle of automatic washing machines.

[0017] The composition of the invention comprises *inter alia* from 3 to 80% (by weight based on the total weight of the composition) of one or more detergents (b).

[0018] The term "detergent" in the context of this invention denotes a surfactant which provides a detergent

(i.e. cleaning) effect to laundry treated as part of a domestic laundering process.

[0019] The choice of deterative surfactant, and the amount present, will depend on the intended use of the detergent composition. For example, different surfactant systems may be chosen for hand-washing products and for products intended for use in different types of automatic washing machine. The total amount of deterative surfactant present will also depend on the intended end use. In compositions for machine washing of fabrics, an amount of from 5 to 40%, such as 15 to 35% (by weight based on the total weight of the composition) is generally appropriate. Higher levels may be used in compositions for washing fabrics by hand, such as up to 60% (by weight based on the total weight of the composition).

[0020] Preferred deterative surfactants may be selected from non-soap anionic surfactants, nonionic surfactants and mixtures thereof.

[0021] Non-soap anionic surfactants are principally used to facilitate particulate soil removal. Non-soap anionic surfactants for use in the invention are typically salts of organic sulfates and sulfonates having alkyl or alkenyl (preferably alkyl) groups containing from about 8 to about 22 (preferably from 10 to 18) carbon atoms, the terms "alkyl" and "alkenyl" being used to include the alkyl or alkenyl portions, respectively, of higher acyl groups. Examples of such materials include alkyl sulfates, alkyl ether sulfates, alkaryl sulfonates, alpha-olefin sulfonates and mixtures thereof, in which the alkyl groups contain from 10 to 18 carbon atoms. The alkyl ether sulfates may contain from one to ten ethylene oxide or propylene oxide units per molecule, and preferably contain one to three ethylene oxide units per molecule. The counterion for anionic surfactants is generally an alkali metal such as sodium or potassium; or an ammoniacal counterion such as monoethanolamine, (MEA) diethanolamine (DEA) or triethanolamine (TEA). Mixtures of such counterions may also be employed.

[0022] A preferred class of non-soap anionic surfactant for use in the invention includes alkylbenzene sulfonates, particularly linear alkylbenzene sulfonates (LAS) with a linear alkyl group having an alkyl chain length of from 10 to 18 carbon atoms. Commercial LAS is a mixture of closely related isomers and alkyl chain homologues, each containing an aromatic ring sulfonated at the "para" position and attached to a linear alkyl group at any position except the terminal carbons. The linear alkyl group typically has an alkyl chain length of from 11 to 15 carbon atoms, with the predominant materials having a chain length of about C12. Each alkyl chain homologue consists of a mixture of all the possible sulfophenyl isomers except for the 1-phenyl isomer. LAS is normally formulated into compositions in acid (i.e. HLAS) form and then at least partially neutralized in-situ.

[0023] Also suitable are alkyl ether sulfates having a straight or branched chain alkyl group having 10 to 18, more preferably 12 to 14 carbon atoms and containing an average of 1 to 3EO units per molecule. A preferred example is sodium lauryl ether sulfate (SLES) in which the predominantly C12 lauryl alkyl group has been ethoxylated with an average of 3EO units per molecule.

[0024] Some alkyl sulfate surfactant (PAS) may be used, such as non-ethoxylated primary and secondary alkyl sulfates with an alkyl group having an alkyl chain length of from 10 to 18.

[0025] Mixtures of any of the above described materials may also be used. A preferred mixture of non-soap anionic surfactants for use in the invention comprises linear alkylbenzene sulfonate (preferably C₁₁ to C₁₅ linear alkyl benzene sulfonate) and sodium lauryl ether sulfate (preferably C₁₀ to C₁₈ alkyl sulfate ethoxylated with an average of 1 to 3 EO).

[0026] In a detergent composition according to the invention, the total level of non-soap anionic surfactant may suitably range from 5 to 30% (by weight based on the total weight of the composition).

[0027] Nonionic surfactants may provide enhanced performance for removing very hydrophobic oily soil and for cleaning hydrophobic polyester and polyester/cotton blend fabrics. Nonionic surfactants for use in the invention are typically polyoxyalkylene compounds, i.e. the reaction product of alkylene oxides (such as ethylene oxide or propylene oxide or mixtures thereof) with starter molecules having a hydrophobic group and a reactive hydrogen atom which is reactive with the alkylene oxide. Such starter molecules include alcohols, acids, amides or alkyl phenols. Where the starter molecule is an alcohol, the reaction product is known as an alcohol alkoxylate. The polyoxyalkylene compounds can have a variety of block and heteric (random) structures. For example, they can comprise a single block of alkylene oxide, or they can be diblock alkoxylates or triblock alkoxylates. Within the block structures, the blocks can be all ethylene oxide or all propylene oxide, or the blocks can contain a heteric mixture of alkylene oxides. Examples of such materials include aliphatic alcohol ethoxylates such as C₈ to C₁₈ primary or secondary linear or branched alcohol ethoxylates with an average of from 2 to 40 moles of ethylene oxide per mole of alcohol.

[0028] A preferred class of nonionic surfactant for use in the invention includes aliphatic C₈ to C₁₈, more preferably C₁₂ to C₁₅ primary linear alcohol ethoxylates with an average of from 3 to 20, more preferably from 5 to 10 moles of ethylene oxide per mole of alcohol.

[0029] Mixtures of any of the above described materials may also be used.

[0030] In a detergent composition according to the invention, the total level of nonionic surfactant may suitably range from 0 to 25% (by weight based on the total weight of the composition).

[0031] A detergent composition of the invention may contain one or more cosurfactants (such as amphoteric (zwitterionic) and/or cationic surfactants) in addition to the non-soap anionic and/or nonionic deterative surfactants described

above.

[0032] Specific cationic surfactants include C8 to C18 alkyl dimethyl ammonium halides and derivatives thereof in which one or two hydroxyethyl groups replace one or two of the methyl groups, and mixtures thereof. Cationic surfactant, when included, may be present in an amount ranging from 0.1 to 5% (by weight based on the total weight of the composition).

[0033] Specific amphoteric (zwitterionic) surfactants include alkyl amine oxides, alkyl betaines, alkyl amidopropyl betaines, alkyl sulfobetaines (sultaines), alkyl glycinate, alkyl carboxyglycinates, alkyl amphotacetates, alkyl amphotpropionates, alkylamphotglycinates, alkyl amidopropyl hydroxysultaines, acyl taurates and acyl glutamates, having alkyl groups containing from about 8 to about 22 carbon atoms, the term "alkyl" being used to include the alkyl portion of higher acyl groups. Amphoteric (zwitterionic) surfactant, when included, may be present in an amount ranging from 0.1 to 5% (by weight based on the total weight of the composition).

[0034] A detergent composition according to the invention may suitably be in liquid or particulate form, or a mixture thereof.

[0035] The term "particulate" in the context of this invention denotes free-flowing or compacted solid forms such as powders, granules, pellets, flakes, bars, briquettes or tablets.

[0036] One preferred form for a particulate detergent composition according to the invention is a free-flowing powdered solid, with a loose (unpacked) bulk density generally ranging from about 200g/l to about 1,300 g/l, preferably from about 400 g/l to about 1,000 g/l, more preferably from about 500g/l to about 900 g/l.

[0037] The detergent composition according to the invention is most preferably in liquid form.

[0038] The term "liquid" in the context of this invention denotes that a continuous phase or predominant part of the composition is liquid, and that the composition is flowable at 15°C and above. Accordingly, the term "liquid" may encompass emulsions, suspensions, and compositions having flowable yet stiffer consistency, known as gels or pastes. The viscosity of the composition may suitably range from about 200 to about 10,000 mPa.s at 25°C at a shear rate of 21 sec⁻¹. This shear rate is the shear rate that is usually exerted on the liquid when poured from a bottle. Pourable liquid compositions generally have a viscosity of from 200 to 2,500 mPa.s, preferably from 200 to 1500 mPa.s.

Liquid compositions which are pourable gels generally have a viscosity of from 1,500 mPa.s to 6,000 mPa.s, preferably from 1,500 mPa.s to 2,000 mPa.s.

[0039] A liquid detergent composition according to the invention may generally comprise from 5 to 95%, preferably from 10 to 90%, more preferably from 15 to 85% water (by weight based on the total weight of the composition). The composition may also incorporate non-aqueous carriers such as hydrotropes, co-solvents and phase stabilizers. Such materials are typically low molecular weight, water-soluble or water-miscible organic liquids such as C1 to C5 monohydric alcohols (such as ethanol and n- or i-propanol); C2 to C6 diols (such as monopropylene glycol and dipropylene glycol); C3 to C9 triols (such as glycerol); polyethylene glycols having a weight average molecular weight (M_w) ranging from about 200 to 600; C1 to C3 alkanolamines such as mono-, di- and triethanolamines; and alkyl aryl sulfonates having up to 3 carbon atoms in the lower alkyl group (such as the sodium and potassium xylene, toluene, ethylbenzene and isopropyl benzene (cumene) sulfonates).

[0040] Mixtures of any of the above described materials may also be used.

[0041] Non-aqueous carriers, when included in a liquid detergent composition according to the invention, may be present in an amount ranging from 0.1 to 20%, preferably from 1 to 15%, and more preferably from 3 to 12% (by weight based on the total weight of the composition).

Builders

[0042] A detergent composition according to the invention may contain one or more builders. Builders enhance or maintain the cleaning efficiency of the surfactant, primarily by reducing water hardness. This is done either by sequestration or chelation (holding hardness minerals in solution), by precipitation (forming an insoluble substance), or by ion exchange (trading electrically charged particles).

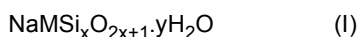
[0043] Builders for use in the invention can be of the organic or inorganic type, or a mixture thereof. Non-phosphate builders are preferred.

[0044] Inorganic, non-phosphate builders for use in the invention include hydroxides, carbonates, silicates, zeolites, and mixtures thereof.

[0045] Suitable hydroxide builders for use in the invention include sodium and potassium hydroxide.

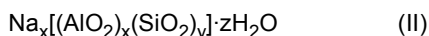
[0046] Suitable carbonate builders for use in the invention include mixed or separate, anhydrous or partially hydrated alkali metal carbonates, bicarbonates or sesquicarbonates. Preferably the alkali metal is sodium and/or potassium, with sodium carbonate being particularly preferred.

[0047] Suitable silicate builders include amorphous forms and/or crystalline forms of alkali metal (such as sodium) silicates. Preferred are crystalline layered sodium silicates (phyllosilicates) of the general formula (I)



in which M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2 or 3 and y is a number from 0 to 20. Sodium disilicates of the above formula in which M is sodium and x is 2 are particularly preferred. Such materials can be prepared with different crystal structures, referred to as α , β , γ and δ phases, with δ -sodium disilicate being most preferred.

[0048] Zeolites are naturally occurring or synthetic crystalline aluminosilicates composed of $(\text{SiO}_4)^{4-}$ and $(\text{AlO}_4)^{5-}$ tetrahedra, which share oxygen-bridging vertices and form cage-like structures in crystalline form. The ratio between oxygen, aluminium and silicon is $\text{O}:(\text{Al} + \text{Si}) = 2:1$. The frameworks acquire their negative charge by substitution of some Si by Al. The negative charge is neutralised by cations and the frameworks are sufficiently open to contain, under normal conditions, mobile water molecules. Suitable zeolite builders for use in the invention may be defined by the general formula (II):



in which x and y are integers of at least 6, the molar ratio of x to y is in the range from about 1 to about 0.5, and z is an integer of at least 5, preferably from about 7.5 to about 276, more preferably from about 10 to about 264.

[0049] Preferred inorganic, non-phosphate builders for use in the invention may be selected from zeolites (of the general formula (II) defined above), sodium carbonate, δ -sodium disilicate and mixtures thereof.

[0050] Suitable organic, non-phosphate builders for use in the invention include polycarboxylates, in acid and/or salt form. When utilized in salt form, alkali metal (e.g. sodium and potassium) or alkanolammonium salts are preferred. Specific examples of such materials include sodium and potassium citrates, sodium and potassium tartrates, the sodium and potassium salts of tartaric acid monosuccinate, the sodium and potassium salts of tartaric acid disuccinate, sodium and potassium ethylenediaminetetraacetates, sodium and potassium N(2-hydroxyethyl)-ethylenediamine triacetates, sodium and potassium nitrilotriacetates and sodium and potassium N-(2-hydroxyethyl)-nitrilotriacetates. Polymeric polycarboxylates may also be used, such as polymers of unsaturated monocarboxylic acids (e.g. acrylic, methacrylic, vinylacetic, and crotonic acids) and/or unsaturated dicarboxylic acids (e.g. maleic, fumaric, itaconic, mesaconic and citraconic acids and their anhydrides). Specific examples of such materials include polyacrylic acid, polymaleic acid, and copolymers of acrylic and maleic acid. The polymers may be in acid, salt or partially neutralised form and may suitably have a molecular weight (Mw) ranging from about 1,000 to 100,000, preferably from about 2,000 to about 85,000, and more preferably from about 2,500 to about 75,000.

[0051] Preferred organic, non-phosphate builders for use in the invention may be selected from polycarboxylates (e.g. citrates) in acid and/or salt form and mixtures thereof.

[0052] Mixtures of any of the above described materials may also be used.

[0053] Preferably the level of phosphate builders in a detergent composition of the invention is no more than 0.2%, preferably from 0 to 0.1%, more preferably from 0 to 0.01% and most preferably 0% (by weight based on the total weight of the composition). The term "phosphate builder" in the context of this invention denotes alkali metal, ammonium and alkanolammonium salts of polyphosphate, orthophosphate, and/or metaphosphate (e.g. sodium tripolyphosphate).

[0054] The overall level of builder, when included, may range from about 0.1 to about 80%, preferably from about 0.5 to about 50% (by weight based on the total weight of the composition).

Transition metal ion sequestrants

[0055] In addition to the 1-hydroxy-1,1-bisphosphonates (a) as described above, a detergent composition according to the invention may contain additional transition metal ion sequestrants. Specific examples of such materials include aminotris(methylene phosphonic acid) (ATMP), 1-hydroxyethylidene diphosphonic acid (HEDP) and diethylenetriamine penta(methylene phosphonic acid) (DTPMP) and their respective sodium or potassium salts. Mixtures of any of the above described materials may also be used.

[0056] However, the level of such additional transition metal ion sequestrants in a detergent composition of the invention is typically no more than 0.2%, preferably from 0 to 0.1%, more preferably from 0 to 0.01% and most preferably 0% (by weight based on the total weight of the composition).

[0057] A particulate detergent composition of the invention may include one or more fillers to assist in providing the desired density and bulk to the composition. Suitable fillers for use in the invention may generally be selected from neutral salts with a solubility in water of at least 1 gram per 100 grams of water at 20° C; such as alkali metal, alkaline earth metal, ammonium or substituted ammonium chlorides, fluorides, acetates and sulfates and mixtures thereof. Preferred fillers for use in the invention include alkali metal (more preferably sodium and/or potassium) sulfates and chlorides and mixtures thereof, with sodium sulfate and/or sodium chloride being most preferred.

[0058] Filler, when included, may be present in a total amount ranging from about 1 to about 80%, preferably from about 5 to about 50% (by weight based on the total weight of the composition).

Polymeric cleaning boosters

[0059] A detergent composition according to the invention may include one or more polymeric cleaning boosters such as antiredeposition polymers, soil release polymers and mixtures thereof.

[0060] Anti-redeposition polymers stabilise the soil in the wash solution thus preventing redeposition of the soil. Suitable anti-redeposition polymers for use in the invention include alkoxyated polyethyleneimines. Polyethyleneimines are materials composed of ethylene imine units $-\text{CH}_2\text{CH}_2\text{NH}-$ and, where branched, the hydrogen on the nitrogen is replaced by another chain of ethylene imine units. Preferred alkoxyated polyethyleneimines for use in the invention have a polyethyleneimine backbone of about 300 to about 10000 weight average molecular weight (M_w). The polyethyleneimine backbone 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. Where a nitrogen atom is alkoxyated, a preferred average degree of alkoxylation is from 10 to 30, preferably from 15 to 25 alkoxy groups per modification. A preferred material is ethoxylated polyethyleneimine, with an average degree of ethoxylation being from 10 to 30, preferably from 15 to 25 ethoxy groups per ethoxylated nitrogen atom in the polyethyleneimine backbone. Another type of suitable anti-redeposition polymer for use in the invention includes cellulose esters and ethers, for example sodium carboxymethyl cellulose.

[0061] Mixtures of any of the above described materials may also be used.

[0062] The overall level of anti-redeposition polymer, when included, may range from 0.05 to 6%, more preferably from 0.1 to 5% (by weight based on the total weight of the composition).

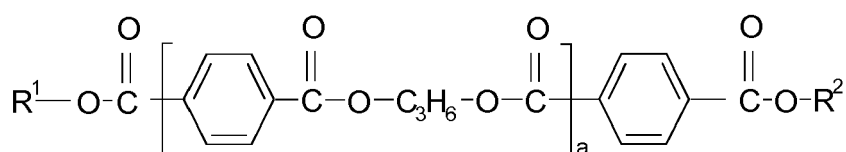
[0063] Soil release polymers help to improve the detachment of soils from fabric by modifying the fabric surface during washing. The adsorption of a SRP over the fabric surface is promoted by an affinity between the chemical structure of the SRP and the target fibre.

[0064] SRPs for use in the invention may include a variety of charged (e.g. anionic) as well as non-charged monomer units and structures may be linear, branched or star-shaped. The SRP structure may also include capping groups to control molecular weight or to alter polymer properties such as surface activity. The weight average molecular weight (M_w) of the SRP may suitably range from about 1000 to about 20,000 and preferably ranges from about 1500 to about 10,000.

[0065] SRPs for use in the invention may suitably be selected from copolyesters of dicarboxylic acids (for example adipic acid, phthalic acid or terephthalic acid), diols (for example ethylene glycol or propylene glycol) and polydiols (for example polyethylene glycol or polypropylene glycol). The copolyester may also include monomeric units substituted with anionic groups, such as for example sulfonated isophthaloyl units. Examples of such materials include oligomeric esters produced by transesterification/oligomerization of poly(ethyleneglycol) methyl ether, dimethyl terephthalate ("DMT"), propylene glycol ("PG") and poly(ethyleneglycol) ("PEG"); partly- and fully-anionic-end-capped oligomeric esters such as oligomers from ethylene glycol ("EG"), PG, DMT and Na-3,6-dioxa-8-hydroxyoctanesulfonate; nonionic-capped block polyester oligomeric compounds such as those produced from DMT, Me-capped PEG and EG and/or PG, or a combination of DMT, EG and/or PG, Me-capped PEG and Na-dimethyl-5-sulfoisophthalate, and copolymeric blocks of ethylene terephthalate or propylene terephthalate with polyethylene oxide or polypropylene oxide terephthalate

[0066] Other types of SRP for use in the invention include cellulosic derivatives such as hydroxyether cellulosic polymers, C_1 - C_4 alkylcelluloses and C_4 hydroxyalkyl celluloses; polymers with poly(vinyl ester) hydrophobic segments such as graft copolymers of poly(vinyl ester), for example C_1 - C_6 vinyl esters (such as poly(vinyl acetate)) grafted onto polyalkylene oxide backbones; poly(vinyl caprolactam) and related co-polymers with monomers such as vinyl pyrrolidone and/or dimethylaminoethyl methacrylate; and polyester-polyamide polymers prepared by condensing adipic acid, caprolactam, and polyethylene glycol.

[0067] Preferred SRPs for use in the invention include copolyesters formed by condensation of terephthalic acid ester and diol, preferably 1,2 propanediol, and further comprising an end cap formed from repeat units of alkylene oxide capped with an alkyl group. Examples of such materials have a structure corresponding to general formula (III):



(III)

in which R^1 and R^2 independently of one another are $\text{X}-(\text{OC}_2\text{H}_4)_n-(\text{OC}_3\text{H}_6)_m$;

in which X is C_{1-4} alkyl and preferably methyl;

n is a number from 12 to 120, preferably from 40 to 50;

m is a number from 1 to 10, preferably from 1 to 7; and

a is a number from 4 to 9.

[0068] Because they are averages, m, n and a are not necessarily whole numbers for the polymer in bulk.

[0069] Mixtures of any of the above described materials may also be used.

[0070] The overall level of SRP, when included, may range from 0.1 to 10%, preferably from 0.3 to 7%, more preferably from 0.5 to 5% (by weight based on the total weight of the composition).

Fatty Acid

[0071] A detergent composition according to the invention may in some cases contain one or more fatty acids and/or salts thereof.

[0072] Suitable fatty acids in the context of this invention include aliphatic carboxylic acids of formula RCOOH , where R is a linear or branched alkyl or alkenyl group containing from 6 to 24, more preferably 10 to 22, most preferably from 12 to 18 carbon atoms and 0 or 1 double bond. Preferred examples of such materials include saturated C12-18 fatty acids such as lauric acid, myristic acid, palmitic acid or stearic acid; and fatty acid mixtures in which 50 to 100% (by weight based on the total weight of the mixture) consists of saturated C12-18 fatty acids. Such mixtures may typically be derived from natural fats and/or optionally hydrogenated natural oils (such as coconut oil, palm kernel oil or tallow). The fatty acids may be present in the form of their sodium, potassium or ammonium salts and/or in the form of soluble salts of organic bases, such as mono-, di- or triethanolamine.

[0073] Mixtures of any of the above described materials may also be used.

[0074] Fatty acids and/or their salts, when included, may be present in an amount ranging from about 0.25 to 5%, more preferably from 0.5 to 5%, most preferably from 0.75 to 4% (by weight based on the total weight of the composition).

[0075] For formula accounting purposes, in the formulation, fatty acids and/or their salts (as defined above) are not included in the level of surfactant or in the level of builder.

Rheology modifiers

[0076] A liquid detergent composition according to the invention may comprise one or more rheology modifiers. Examples of such materials include polymeric thickeners and/or structurants such as hydrophobically modified alkali swellable emulsion (HASE) copolymers. Exemplary HASE copolymers for use in the invention include linear or crosslinked copolymers that are prepared by the addition polymerization of a monomer mixture including at least one acidic vinyl monomer, such as (meth)acrylic acid (i.e. methacrylic acid and/or acrylic acid); and at least one associative monomer. The term "associative monomer" in the context of this invention denotes a monomer having an ethylenically unsaturated section (for addition polymerization with the other monomers in the mixture) and a hydrophobic section. A preferred type of associative monomer includes a polyoxyalkylene section between the ethylenically unsaturated section and the hydrophobic section. Preferred HASE copolymers for use in the invention include linear or crosslinked copolymers that are prepared by the addition polymerization of (meth)acrylic acid with (i) at least one associative monomer selected from linear or branched $\text{C}_8\text{-C}_{40}$ alkyl (preferably linear $\text{C}_{12}\text{-C}_{22}$ alkyl) polyethoxylated (meth)acrylates; and (ii) at least one further monomer selected from $\text{C}_1\text{-C}_4$ alkyl (meth) acrylates, polyacidic vinyl monomers (such as maleic acid, maleic anhydride and/or salts thereof) and mixtures thereof. The polyethoxylated portion of the associative monomer (i) generally comprises about 5 to about 100, preferably about 10 to about 80, and more preferably about 15 to about 60 oxyethylene repeating units.

[0077] Mixtures of any of the above described materials may also be used.

[0078] Polymeric thickeners, when included, may be present in an amount ranging from 0.1 to 5% (by weight based on the total weight of the composition).

[0079] A liquid detergent composition according to the invention may also have its rheology modified by use of one or more external structurants which form a structuring network within the composition. Examples of such materials include hydrogenated castor oil, microfibrinous cellulose and citrus pulp fibre. The presence of an external structurant may provide shear thinning rheology and may also enable materials such as encapsulates and visual cues to be suspended stably in the liquid.

Enzymes

[0080] A detergent composition according to the invention may comprise an effective amount of one or more enzymes selected from the group comprising, pectate lyase, protease, amylase, cellulase, lipase, mannanase and mixtures thereof. The enzymes are preferably present with corresponding enzyme stabilizers.

[0081] A liquid detergent composition according to the invention preferably has a pH in the range of 5 to 9, more

preferably 6 to 8, when measured on dilution of the composition to 1% (by weight based on the total weight of the composition) using demineralised water.

Other Ingredients

[0082] A detergent composition of the invention may contain further optional ingredients to enhance performance and/or consumer acceptability. Examples of such ingredients include fragrance oils, foam boosting agents, preservatives (e.g. bactericides), antioxidants, sunscreens, anticorrosion agents, colorants, pearlisers and/or opacifiers, and shading dye. Each of these ingredients will be present in an amount effective to accomplish its purpose. Generally, these optional ingredients are included individually at an amount of up to 5% (by weight based on the total weight of the composition).

[0083] A detergent composition of the invention generally contains no more than 0.2%, preferably from 0 to 0.1%, more preferably from 0 to 0.01% and most preferably 0% (by weight based on the total weight of the composition) of transition metal ions selected from Fe (III), Co (II), Co (III), Mn (II), Mn (III), Ce (III), Ce (IV), Zn (II) and Bi (III) and mixtures thereof.

[0084] A detergent composition of the invention generally contains no more than 0.2%, preferably no more than 0.1%, more preferably no more than 0.01% and most preferably 0% (by weight based on the total weight of the composition) of oxidising agents selected from halogen-based bleaches (e.g. alkali metal hypochlorites and alkali metal salts of di- and tri-chloro and di- and tri-bromo cyanuric acids), oxygen-based bleaches (e.g. sodium perborate (tetra- or monohydrate), sodium percarbonate and hydrogen peroxide) and mixtures thereof.

Packaging and dosing

[0085] The detergent composition of the invention may be packaged as unit doses in polymeric film soluble in the wash water. Alternatively, the detergent composition of the invention may be supplied in multidose plastics packs with a top or bottom closure. A dosing measure may be supplied with the pack either as a part of the cap or as an integrated system.

[0086] A method for the non-oxidative laundering of fabric stains using a detergent composition according to the invention comprises diluting a dose of the detergent composition to obtain a wash liquor and washing the stained fabric with the wash liquor so formed.

[0087] The method may suitably be carried out in a top-loading or front-loading automatic washing machine or can be carried out by hand.

[0088] In automatic washing machines, the dose of detergent composition is typically put into a dispenser and from there it is flushed into the machine by the water flowing into the 5 machines, thereby forming the wash liquor. Dosages for a typical front-loading washing machine (using 10 to 15 litres of water to form the wash liquor) may range from about 10 ml to about 100 ml, preferably about 15 to 75 ml. Dosages for a typical top-loading washing machine (using from 40 to 60 litres of water to form the wash liquor) may be higher, e.g. 100 ml or more. Lower dosages of detergent (e.g. 50 ml or less) may be 10 used for hand washing methods (using about 1 to 10 litres of water to form the wash liquor).

[0089] A subsequent aqueous rinse step and drying the laundry is preferred. Any input of water during any optional rinsing step(s) is not included when determining the volume of the wash liquor. Laundry drying can take place either in an automatic dryer or in the open air.

[0090] The invention will now be further described with reference to the following non-limiting Examples.

EXAMPLES

[0091] All weight percentages are by weight based on total weight unless otherwise specified.

[0092] Liquid laundry detergent formulations were prepared by sequential mixing of the ingredients as shown in Table 1.

[0093] Compositions according to the invention are indicated by a number; and comparative examples (not according to the invention) are indicated by a letter.

Table 1

Ingredient	wt.% (active ingredient)						
	Example						
Formulation	A	B	C	D	1	2	3
Glycerol	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Alcohol ethoxylate	4.3	4.3	4.3	4.3	4.3	4.3	4.3

(continued)

Ingredient	wt.% (active ingredient)						
Formulation	Example						
	A	B	C	D	1	2	3
LAS acid	5.8	5.8	5.8	5.8	5.8	5.8	5.8
TEA	8.8	8.8	8.8	8.8	8.8	8.8	8.8
Lauric acid	0.9	0.9	0.9	0.9	0.9	0.9	0.9
SLES 1 EO	4.4	4.4	4.4	4.4	4.4	4.4	4.4
Preservative	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Sequestrant ⁽¹⁾	-	0.5	1.0	1.5	-	-	-
Sequestrant ⁽²⁾	-	-	-	-	0.5	1.0	1.5
Water	q.s. to 100						
⁽¹⁾ Dequest®2010 (HEDP)							
⁽²⁾ (1,6-dihydroxy-1,6,6-triphosphonohexyl) phosphonic acid							

[0094] The formulations were evaluated for their cleaning performance at 30°C using a Heraeus 12-pot Linitester to mimic the mechanical action of a front-loading automatic washing machine.

[0095] Hard model wash water (a) was prepared by dissolving 0.235g calcium chloride dihydrate and 0.163g magnesium chloride hexahydrate into 1 litre of demineralised water to give 24° FH hardness and a 2:1 calcium to magnesium ratio.

[0096] Hard, transition metal doped model wash water (b) was prepared by first dissolving 5.18 g of ammonium iron (III) sulphate dodecahydrate, 1.298 g of copper (II) sulphate pentahydrate, 3.034 g of zinc sulphate heptahydrate and 0.111 g manganese sulphate monohydrate in 0.5 litres of demineralized water, then acidifying the solution to pH 1.0 by dropwise addition of concentrated sulfuric acid. 2.5 ml of the acidified solution was then added to 3 litres of hard model wash water (a), immediately prior to use.

[0097] Test wash liquors were prepared by diluting 2.9 g of the selected test formulation in 1 litre of hard, transition metal doped water (b), and dosing a 100 ml aliquot of the test wash liquor into the Linitest pot. 2.0 cm x 2.0 cm swatches of black tea stained cotton and 20 cm x 20 cm swatches of unstained cotton ballast were placed into each Linitest pot. The pots were sealed and attached to the Linitester cradle and rotated at 40 rpm for 30 minutes at 30°C.

[0098] The swatches were then removed from the pots and wrung out by hand to drain residual test wash liquor. The Linitest pots were rinsed and 100 ml of water was added. The swatches were returned to the pots and rinsed for 5 minutes. The swatches were then removed, wrung out and the rinse water drained and replaced with fresh water before returning the swatches to the pot and carrying out a second 5-minute rinse. The swatches were placed on laboratory paper towel and allowed to air dry in the open laboratory.

[0099] The extent of black tea stain removal was measured by making diffuse reflectance measurements using a spectrometer, and expressed as the Stain Removal Index (SRI), defined as:

$SRI = 100 - \Delta E$, where ΔE is the difference in colour of the stained cloth compared to an unstained cloth.

[0100] A higher SRI value indicates cleaner swatches. Three replicate swatches were measured for each test wash liquor. The results are shown in Table 2.

Table 2

Formulation used in test wash liquor	SRI
A (control)	83.39 ± 0.26
B	86.83 ± 0.28
C	87.45 ± 0.14
D	86.94 ± 0.12
1	87.45 ± 0.22
2	87.52 ± 0.10
3	88.06 ± 0.09

[0101] The testing was repeated using the same protocol, but with red wine stained cotton swatches in place of the black tea stained cotton swatches. The results are shown in Table 3.

Table 3

Formulation used in test wash liquor	SRI
A (control)	90.08 \pm 0.19
B	92.46 \pm 0.15
C	91.89 \pm 0.42
D	92.24 \pm 0.59
1	92.98 \pm 0.30
2	93.06 \pm 0.31
3	93.62 \pm 0.35

[0102] The results show that Examples 1 to 3 according to the invention (with (1,6-dihydroxy-1,6,6-triphosphohexyl) phosphonic acid) provide superior performance on the black tea and red wine stains compared to the comparative examples B to D (with Dequest®2010).

Claims

1. A detergent composition for the non-oxidative laundering of fabric stains, the composition comprising:
 - (a) from 0.1 to 10% (by weight based on the total weight of the composition) of (1,6-dihydroxy-1,6,6-triphosphohexyl) phosphonic acid and/or a salt thereof; and
 - (b) from 3 to 80% (by weight based on the total weight of the composition) of one or more deterative surfactants.
2. A composition according to claim 1, in which the salt of (1,6-dihydroxy-1,6,6-triphosphohexyl) phosphonic acid is selected from those where one or more of the acidic hydrogen atoms in the molecule are replaced by an alkali metal or ammoniacal cation.
3. A composition according to claim 2, in which the salt of (1,6-dihydroxy-1,6,6-triphosphohexyl) phosphonic acid is selected from those where one or more of the acidic hydrogen atoms in the molecule are replaced by sodium.
4. A composition according to any one of claims 1 to 3, in which the total amount of (1,6-dihydroxy-1,6,6-triphosphohexyl) phosphonic acid and/or salt thereof ranges from 1 to 5% (by weight based on the total weight of the composition).
5. A composition according to any one of claims 1 to 4, in which the one or more deterative surfactants (b) are selected from non-soap anionic surfactants, nonionic surfactants and mixtures thereof.
6. A composition according to any preceding claim which contains no more than 0.2%, preferably from 0 to 0.1%, more preferably from 0 to 0.01% and most preferably 0% (by weight based on the total weight of the composition) of transition metal ions selected from Fe (III), Co (II), Co (III), Mn (II), Mn (III), Ce (III), Ce (IV), Zn (II) and Bi (III) and mixtures thereof.
7. A composition according to any preceding claim which contains no more than 0.2%, preferably no more than 0.1%, more preferably no more than 0.01% and most preferably 0% (by weight based on the total weight of the composition) of oxidising agents selected from halogen-based bleaches (e.g. alkali metal hypochlorites and alkali metal salts of di- and tri-chloro and di- and tri-bromo cyanuric acids), oxygen-based bleaches (e.g. sodium perborate (tetra- or monohydrate), sodium percarbonate and hydrogen peroxide) and mixtures thereof.
8. A method for the non-oxidative laundering of fabric stains, comprising diluting a dose of the detergent composition as defined in any one of claims 1 to 7 to obtain a wash liquor, and washing the stained fabric with the wash liquor so formed.



EUROPEAN SEARCH REPORT

 Application Number
 EP 18 20 5044

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EPO FORM 1503 03.82 (P04C01)

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
Y	EP 0 001 853 A1 (PROCTER & GAMBLE [US]) 16 May 1979 (1979-05-16) * page 11, paragraph 2; claim 1 * * page 25, last paragraph * -----	1-8	INV. C11D3/36 C11D11/00
Y	JEAN-PAUL SILVESTRE ET AL: "SYNTHÈSE ET ÉTUDE STRUCTURALE D'ACIDES DIHYDROXYTÉTRAPHOSPHONIQUES ET DE SELS DE CES ACIDES. III: UN CAS D'ISOMORPHISME ENTRE LE SEL DE POTASSIUM ET L'ACIDE 1,6-DIHYDROXYHEXYLIDÈNE-1,1,6,6-TÉTRAPHOSPHONIQUE (DHHTP) HYDRATÉ", PHOSPHORUS, SULFUR AND SILICON AND THE RELATED ELEMENTS, vol. 170, no. 1, 27 March 2001 (2001-03-27), pages 91-113, XP055572222, US ISSN: 1042-6507, DOI: 10.1080/10426500108040588 * page 92, paragraph 1 * -----	1-8	TECHNICAL FIELDS SEARCHED (IPC)
Y	US 3 584 035 A (NICHOLSON DENZEL ALLAN ET AL) 8 June 1971 (1971-06-08) * column 25, lines 55-60 * * column 27, lines 43-62 * * column 3, lines 29-35 * * column 5, lines 33-38 * -----	1-8	C11D
Y	GB 1 596 756 A (PROCTER & GAMBLE LTD) 26 August 1981 (1981-08-26) * page 2, lines 6-13 * * page 7, line 17 * -----	1-8	
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 21 March 2019	Examiner Gault, Nathalie
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 18 20 5044

5 This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

21-03-2019

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0001853 A1	16-05-1979	DE 2861903 D1 EP 0001853 A1 IT 1100076 B	05-08-1982 16-05-1979 28-09-1985
US 3584035 A	08-06-1971	NONE	
GB 1596756 A	26-08-1981	BE 866245 A GB 1596756 A	23-10-1978 26-08-1981