



(51) International Patent Classification:

C11D 3/30 (2006.01) C11D 3/48 (2006.01)
C11D 3/36 (2006.01)

(21) International Application Number:

PCT/EP2017/062562

(22) International Filing Date:

24 May 2017 (24.05.2017)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

16171744.2 27 May 2016 (27.05.2016) EP

(71) **Applicant** (for AE, AG, AU, BB, BH, BN, BW, BZ, CA, CY, EG, GB, GD, GH, GM, IE, IL, IN, KE, KN, KW, LC, LK, LS, MT, MW, MY, NA, NG, NZ, OM, PG, QA, RW, SA, SC, SD, SG, SL, SZ, TT, TZ, UG, VC, ZA, ZM, ZW only): **UNILEVER PLC** [GB/GB]; a company registered in England and Wales under company no. 41424 of Unilever House, 100 Victoria Embankment, London Greater London EC4Y 0DY (GB).

(71) **Applicant** (for all designated States except AE, AG, AU, BB, BH, BN, BW, BZ, CA, CY, EG, GB, GD, GH, GM, IE, IL, IN, KE, KN, KW, LC, LK, LS, MT, MW, MY, NA, NG, NZ, OM, PG, QA, RW, SA, SC, SD, SG, SL, SZ, TT, TZ, UG, US, VC, ZA, ZM, ZW): **UNILEVER N.V.** [NL/NL]; Weena 455, 3013 AL Rotterdam (NL).

(71) **Applicant** (for US only): **CONOPCO, INC., D/B/A UNILEVER** [US/US]; 800 Sylvan Avenue AG West, S. Wing, Englewood Cliffs, New Jersey 07632 (US).

(72) **Inventors**: **HALL, Caroline, Alexandra**; Unilever R&D Port Sunlight Quarry Road East, Bebington, Wirral Merseyside CH63 3JW (GB). **PARRY, Matthew, Lloyd**; Unilever R&D Port Sunlight Quarry Road East, Bebington, Wirral Merseyside CH63 3JW (GB).

(74) **Agent**: **NEWBOULD, Frazer, Anthony**; Unilever PLC Colworth House, Sharnbrook, Bedford Bedfordshire MK44 1LQ (GB).

(81) **Designated States** (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG,

MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))
- of inventorship (Rule 4.17(iv))

Published:

- with international search report (Art. 21(3))

(54) Title: LAUNDRY COMPOSITION

(57) **Abstract**: The invention relates to an aqueous laundry liquid detergent composition comprising: - a) from 4 to 50 wt.% of one or more surfactants; b) from 0.1 to 5 wt.% of one or more sequestrants, said sequestrants are phosphonic acids and/or salts thereof; c) from 1 to 20 wt.% of triethanolamine; d) from 25 to 94 wt.% of water; wherein if the composition comprises sulfites, they are present at a level of less than 0.1 wt.%; and, wherein if other alkanolamines are present, then the weight ratio of triethanolamine to the sum of other alkanolamines is greater than 12:1.

LAUNDRY COMPOSITION

Field of the Invention

5

This invention relates to a laundry composition. More particularly the invention relates to an aqueous liquid laundry detergent.

Background of the Invention

With the move in laundry detergents to lower active levels of surfactant, there has been in rise in the wish to use more weight efficient ingredients to effect the laundering of clothes. One such useful material are the phosphonic acid sequestrants.

15

However we have found that there is a problem with these materials if sodium is used to neutralise the formulation. Sodium salt crystals of the phosphonate can precipitate out of the formulation.

20

Summary of the Invention

We have found that neutralising with an alkanolamine overcomes the problem that some phosphonate sequestrants will tend to precipitate out of the formulation when using sodium. However when using alkanolamines in a low sulfite, or sulfite free formulation, some alkanolamines have a tendency to yellow. This is seen particularly with monoethanolamine. We have found that by using a particular alkanolamine, triethanolamine, in particular when triethanolamine is the main alkanolamine species present, then this yellowing is reduced, or stopped altogether. Typically, yellowing is seen when the alkanolamine is one which requires a sulphite, for example MEA, and in formulations which require a preservative, i.e. formulations which have high water content. Formulations with low water content, for example, less than 35% wt water, are considered self-preserving. The invention relates solely to formulations which require an isothiazoline preservative, i.e. are high water content.

35

According to the present invention there is provided an aqueous laundry liquid detergent composition according to claim 1.

5 If other alkanolamines are present, then preferably the weight ratio of triethanolamine to the sum of other alkanolamines is greater than 16:1, preferably at least 20:1, more preferably triethanolamine is the sole alkanolamine present, and most preferably triethanolamine is the sole neutralising species present in the formulation.

Preferably the composition is free from sulfites.

10

The phosphonic acid (or salt thereof) sequestrant is preferably selected from the group consisting of: 1-Hydroxyethylidene-1,1-diphosphonic acid (HEDP);

Diethylenetriaminepenta(methylenephosphonic acid) (DTPMP);

Hexamethylenediaminetetra(methylenephosphonic acid) (HDTMP);

15 Aminotris(methylenephosphonic acid) (ATMP);

Ethylenediaminetetra(methylenephosphonic acid) (EDTMP);

Tetramethylenediaminetetra(methylenephosphonic acid) (TDTMP); and,

Phosphonobutanetricarboxylic acid (PBTC).

20 The sequestrant is preferably in acid form. This means that it is a phosphonic acid.

The preferred phosphonic acid sequestrant is 1-Hydroxyethylidene-1,1-diphosphonic acid (HEDP).

25 The surfactant is preferably present at a level of 5 to 40 wt.%, more preferably from 6 to 30 wt.%. A preferred surfactant system comprises the anionic surfactants linear alkylbenzene sulfonate and sodium lauryl ether sulfate as well as the nonionic surfactant alcohol ethoxylate.

30 The composition preferably comprises 0.05 to 6 wt.%, preferably from 0.1 to 5 wt.% of one or more polyester soil release polymer(s).

Preferably the composition comprises from 0.25 to 8 wt.%, preferably from 0.5 to 6 wt.% of an alkoxyated polyethyleneimine. Preferably the alkoxyated polyethyleneimine is an

35 ethoxylated polyethyleneimine.

The composition preferably comprises from 0.0001 to 1 wt.%, preferably from 0.001 to 0.5 wt.%, more preferably from 0.001 to 0.25 wt.% of an isothiazolinone preservative. Preferably the isothiazolinone is benzisothiazolinone and/or methylisothiazolinone.

- 5 A preferred aqueous laundry liquid detergent composition comprises:-
- a) from 6 to 30 wt.% of a surfactant system comprising linear alkylbenzene sulfonate, sodium lauryl ether sulfate, and alcohol ethoxylate;
 - b) from 0.5 to 2.5 wt.% of 1-Hydroxyethylidene-1,1-diphosphonic acid (HEDP);
 - c) from 5 to 16 wt.% of triethanolamine;
 - 10 d) from 25 to 94 wt.% of water;
 - e) from 0.5 to 6 wt.% of an ethoxylated polyethyleneimine;
 - f) from 0.1 to 5 wt.% of one or more polyester soil release polymer(s);
 - g) from 0.001 to 0.25 wt.% of a benzisothiazolinone and/or methylisothiazolinone preservative;
- 15 wherein if the composition comprises sulfites, they are present at a level of less than 0.1 wt.%, preferably less than 0.01 wt.%, more preferably less than 0.001 wt.%; and, wherein if other alkanolamines are present, then the weight ratio of triethanolamine to the sum of other alkanolamines is greater than 12:1.
- 20 The aqueous liquid may preferably comprise one or more hydrophobically modified alkali swellable emulsion (HASE) copolymers, which may be linear in nature or crosslinked.

The composition may optionally, but preferably further comprise one or more of the following ingredients: structurants, foam boosting agents, bactericides, pH buffering

25 agents, polyelectrolytes, anti-shrinking agents, anti-wrinkle agents, anti-oxidants, sunscreens, anti-corrosion agents, drape imparting agents, anti-static agents, ironing aids, colorants, pearlisers, opacifiers, and shading dye.

30 **Detailed Description of the Invention**

Surfactants

The composition comprises surfactant at a level of from 4 to 50 wt.%. Preferably surfactant is included at a level of from 5 to 40 wt.%, more preferably from 6 to 30 wt.%.

The surfactant system may comprise one or more anionic, nonionic, cationic and amphoteric (zwitterionic) surfactants.

Suitable anionic surfactant compounds which may be used can be salts of organic sulfates and sulfonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher acyl radicals. Examples of suitable synthetic anionic surfactant compounds are alkyl sulfates, especially those obtained by sulfating higher C₈ to C₁₈ alcohols, produced for example from tallow or coconut oil, alkyl C₉ to C₂₀ benzene sulfonates, particularly linear secondary alkyl C₁₀ to C₁₅ benzene sulfonates; and alkyl glyceryl ether sulfates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum.

The surfactant preferably comprises anionic surfactant. Preferred anionic surfactant compounds comprise C₁₁ to C₁₅ linear alkyl benzene sulfonate, and C₁₀ to C₁₈ alkyl sulfate ethoxylated with an average of 1 to 3 EO.

Suitable nonionic detergent compounds which may be used include, in particular, the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example, aliphatic alcohols, acids, amides or alkyl phenols with alkylene oxides, especially ethylene oxide either alone or with propylene oxide. Specific nonionic detergent compounds are C₆ to C₂₂ alkyl phenol-ethylene oxide condensates, generally 5 to 25 EO, i.e. 5 to 25 units of ethylene oxide per molecule, and the condensation products of aliphatic C₈ to C₁₈ primary or secondary linear or branched alcohols with ethylene oxide, generally 5 to 40 EO.

The nonionic surfactant preferably comprises alcohol ethoxylate. The alcohol ethoxylates are formed from the reaction of primary or secondary alcohols with ethylene oxide. Typically an aliphatic C₈ to C₁₈ primary or secondary linear or branched alcohol is reacted with ethylene oxide in the required molar amount to produce the alcohol ethoxylate. Preferred alcohol ethoxylates have from 2 to 40, preferably from 3 to 30, more preferably from 5 to 20 ethylene oxide units attached to the aliphatic chain.

Other surfactants such as amphoteric (zwitterionic) and cationic surfactants may also be present.

A preferred surfactant system comprises the anionic surfactants linear alkylbenzene sulfonate and sodium lauryl ether sulfate as well as the nonionic surfactant alcohol ethoxylate. Preferably the surfactant system comprises C₁₁ to C₁₅ linear alkyl benzene sulfonate, C₁₀ to C₁₈ alkyl sulfate ethoxylated with an average of 1 to 3 EO, and an
5 ethoxylated alcohol which is a C₈ to C₁₈ alcohol ethoxylated with from 5 to 20 moles of EO.

Sequestrant

The composition comprises from 0.1 to 5 wt.%, preferably from 0.25 to 4 wt.%, more
10 preferably from 0.5 to 2.5 wt.% of one or more sequestrants. The sequestrant is a phosphonic acid or a salt thereof.

The phosphonic acid (or salt thereof) sequestrant is preferably selected from the group consisting of: 1-Hydroxyethylidene-1,1-diphosphonic acid (HEDP);
15 Diethylenetriaminepenta(methylenephosphonic acid) (DTPMP);
Hexamethylenediaminetetra(methylenephosphonic acid) (HDTMP);
Aminotris(methylenephosphonic acid) (ATMP);
Ethylenediaminetetra(methylenephosphonic acid) (EDTMP);
Tetramethylenediaminetetra(methylenephosphonic acid) (TDTMP); and,
20 Phosphonobutanetricarboxylic acid (PBTC).

It is preferable that the sequestrant is added to the formulation in acid form.

Preferred phosphonic acid sequestrants are 1-Hydroxyethylidene-1,1-diphosphonic acid
25 (HEDP), commercially available as Dequest® 2010; and
Diethylenetriaminepenta(methylenephosphonic acid) (DTPMP), commercially available as Dequest® 2066. The most preferred sequestrant is 1-Hydroxyethylidene-1,1-diphosphonic acid (HEDP).

Triethanolamine

The composition comprises from 1 to 20 wt.%, preferably from 2 to 18 wt.%, more preferably from 4 to 16 wt.%, of triethanolamine. Further preferred levels of triethanolamine may range from 5 to 16 wt.%, and 6 to 16 wt.%.

35 Triethanolamine is an alkanolamine, and is present to neutralise the acids present in the formulation and to provide the correct pH of the composition.

The composition preferably has a pH of between 7 to 8.

We have found that neutralising with an alkanolamine overcomes the problem that some phosphonate sequestrants will tend to precipitate out of solution when using sodium.

- 5 However when using alkanolamines in a low sulfite, or sulfite free formulation, some alkanolamines have a tendency to yellow. This is seen particularly with monoethanolamine. We have found that by using a particular alkanolamine, triethanolamine, this yellowing is reduced.
- 10 If other alkanolamines are present, then the weight ratio of triethanolamine to the sum of other alkanolamines is greater than 12:1. Preferably the weight ratio of triethanolamine to the sum of other alkanolamines is greater than 16:1, more preferably at least than 20:1, most preferably at least 30:1.
- 15 It is preferred that triethanolamine is the sole alkanolamine present, and most preferably triethanolamine is the sole neutralising species present in the formulation. It is preferred if monoethanolamine and any alkali metal (or salt version thereof) is absent from the formulation.

20 Aqueous composition

The composition is an aqueous laundry liquid. Water is present at a level of from 25 to 94 wt.%.

- The aqueous composition can take the form of an isotropic liquid, or it can be a structured
25 liquid using an external structurant.

Sulfites

- If the composition comprises sulfites (for example sodium sulfite), then they are present at a level of less than 0.1 wt.%, preferably less than 0.01 wt.%, more preferably less than
30 0.001 wt.%. It is most preferred that the composition is free from sulfites.

Other preferred ingredients

Fatty Acid

- The composition preferably comprises from 0.25 to 5 wt.%, more preferably from 0.5 to
35 5 wt.%, most preferably from 0.75 to 4 wt.% of fatty acid or salt thereof. Examples include C₆-C₂₂ fatty acids and salts thereof. For the purposes of interpreting the level of

surfactant present in the formulation, fatty acid and their salts are not included in the level of surfactant.

Soil release polymer

- 5 The composition may optionally, but preferably comprise from 0.05 to 6 wt.%, preferably from 0.1 to 5 wt.% of one or more polyester soil release polymer(s). Suitable polyester based soil release polymers are described in WO 2014/029479 and WO 2016/005338.

Alkoxyated polyethylenimine

- 10 The composition preferably comprises from 0.25 to 8 wt.%, preferably from 0.5 to 6 wt.% of an alkoxyated polyethyleneimine. Another preferred level is from 1 to 4 wt.%.

- The polyethyleneimine 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
15 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. A preferred material is ethoxyated polyethyleneimine, with an average degree of ethoxylation being from 10 to 30 preferably from 15 to 25, where a nitrogen atom is ethoxyated.

20 Preservative

The composition comprises a preservative. Preferably the composition comprises from 0.0001 to 1 wt.%, preferably from 0.001 to 0.5 wt.%, more preferably from 0.001 to 0.25 wt.% of a preservative.

- 25 Preferably the composition comprises from 0.0001 to 1 wt.%, preferably from 0.001 to 0.5 wt.%, more preferably from 0.001 to 0.25 wt.% of an isothiazolinone preservative. The preferred isothiazolinone preservatives are benzisothiazolinone and/or methylisothiazolinone. These are commercially available as Proxel® GXL and Neolone® 950.

30

Thickening polymer

- The composition may comprise a thickening polymer. If it does, then preferably the thickening polymer comprises a hydrophobically modified alkali swellable emulsion (HASE) copolymer. The copolymer may be linear in nature or crosslinked. If present,
35 then preferably the thickening polymer is present at a level of from 0.1 to 5 wt.%.

Hydrophobically modified alkali swellable emulsion (HASE) copolymers are known as synthetic associative thickeners. These copolymers typically contain a backbone comprising a major part of residues of randomly distributed methacrylic acid (MAA) and ethylacrylate (EA) monomers. Inserted into this backbone are a small proportion of hydrophobically modified groups, usually less than 3 mol%. The monomers to form these hydrophobic groups are sometimes referred to as surfmers or associative monomers. Due to its structure, the copolymer, when dissolved in an alkaline aqueous liquid, induces a variety of interacting forces such as hydrophobic, hydrogen bonding, electrostatic, etc and this modifies the rheology of the liquid. It is further known that the HASE copolymers and their thickening behaviour may be further modified by use of crosslinkers. HASE copolymers are usually synthesized via emulsion polymerization.

Preferred hydrophobically modified alkali swellable emulsion (HASE) copolymers are made up of the addition polymerisation of: a) unsaturated diacid or an unsaturated cyclic anhydride precursor of such an ethylenically unsaturated diacid; b) acrylic acid or methacrylic acid; c) C₁-C₈ alkyl ester of acrylic acid or methacrylic acid; and, d) a surfmer which is a hydrophobic material which is an unsaturated alkoxyated ester, preferably with 15 to 35 alkoxy groups and an alkyl chain length of > 10 carbon atoms. The copolymer may additionally comprise a crosslinking agent to make a crosslinked thickening polymer.

Fluorescer

The composition may optionally, but preferably comprise a fluorescer. If present, then preferably the composition comprises from 0.005 to 2 wt.%, preferably from 0.01 to 1 wt.%, more preferably from 0.1 to 0.5 wt.% of a fluorescer.

Preferred fluorescers are diamino stilbene disulfonic acid fluorescers. The fluorescer is preferably of the diamino stilbene disulfonic acid cyanuric chloride type. In these materials, the diamino stilbene disulfonic acid is reacted with cyanuric chloride to provide the fluorescer material. An example of a preferred fluorescer is Tinopal® 5BM-GX available from BASF.

Other ingredients

The composition may further comprise one or more of the following ingredients: structurants, foam boosting agents, bactericides, pH buffering agents, polyelectrolytes, anti-shrinking agents, anti-wrinkle agents, anti-oxidants, sunscreens, anti-corrosion

agents, drape imparting agents, anti-static agents, ironing aids, colorants, pearlisers, opacifiers, and shading dye.

Hydrotrope

- 5 The liquid detergent composition may optionally include a hydrotrope, which can prevent liquid crystal formation. The addition of the hydrotrope thus aids the clarity/transparency of the composition. Suitable hydrotropes include but are not limited to propylene glycol and glycerol.

Enzymes

- 10 The detergent composition may comprise an effective amount of at least one enzyme selected from the group comprising, pectate lyase, protease, amylase, cellulase, lipase, mannanase. Advantageously it comprises at least 2 of this group of enzymes, more advantageously at least 3 and most advantageously at least 4 of the enzymes from this group.
- 15

Enzyme Stabilizers

- Any enzyme present in the composition may be stabilized using conventional stabilizing agents, e.g., a polyol for example propylene glycol or glycerol, a sugar or sugar alcohol, lactic acid, boric acid, or a boric acid derivative, e.g., an aromatic borate ester, or a phenyl boronic acid derivative for example 4-formylphenyl boronic acid, and the composition may be formulated as described in e.g. WO 92/19709 and WO 92/19708.
- 20

Lignin compounds

- 25 When a lipase enzyme is included a lignin compound may be used in the composition in an amount that can be optimised by trial and error. Lignin is a component of all vascular plants, found mostly between cellular structures but also within the cells and in the cell walls.
- 30 Preferably the lignin compound comprises a lignin polymer and more preferably it is a modified lignin polymer. A modified lignin polymer as used herein is lignin that has been subjected to a chemical reaction to attach chemical moieties to the lignin covalently. The attached chemical moieties are preferably randomly substituted.

Bleach Catalyst

Compositions may comprise a weight efficient bleach system. Such systems typically do not utilise the conventional percarbonate and bleach activator approach. An air bleach catalyst system is preferred. Suitable complexes and organic molecule (ligand)

precursors for forming complexes are available to the skilled worker, for example, from: WO 98/39098; WO 98/39406, WO 97/48787, WO 00/29537; WO 00/52124, and WO 00/60045, incorporated by reference. An example of a preferred catalyst is a transition metal complex of MeN4Py ligand (N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane). Suitable bispidon catalyst materials and their action are described in WO 02/48301. The bleach catalyst may be encapsulated to reduce interaction with other components of the liquid during storage.

Photobleaches may also be employed. A "photobleach" is any chemical species that forms a reactive bleaching species on exposure to sunlight, and preferably is not permanently consumed in the reaction. Preferred photo-bleaches include singlet oxygen photo-bleaches and radical photo-bleaches. Suitable singlet oxygen photo-bleaches may be selected from, water soluble phthalocyanine compounds, particularly metallated phthalocyanine compounds where the metal is Zn or Al-Z1 where Z1 is a halide, sulphate, nitrate, carboxylate, alkanolate or hydroxyl ion. Preferably the phthalocyanin has 1-4 SO₃X groups covalently bonded to it where X is an alkali metal or ammonium ion. Such compounds are described in WO 2005/014769 (Ciba).

When present, the bleach catalyst is typically incorporated at a level of about 0.0001 to about 10 wt.%, preferably about 0.001 to about 5 wt.%

Perfume

The composition may optionally, but preferably comprise a perfume. The perfume may be present as a free oil, or it may be an encapsulated perfume. A preferred level of inclusion of perfume is from 0.1 to 3 wt.%.

When the composition is used at very low levels of product dosage, it is advantageous to ensure that perfume is employed efficiently.

A particularly preferred way of ensuring that perfume is employed efficiently is to use an encapsulated perfume. Use of a perfume that is encapsulated reduces the amount of perfume vapour that is produced by the composition before it is diluted. This is important

when the perfume concentration is increased to allow the amount of perfume per wash to be kept at a reasonably high level.

It is even more preferable that the perfume is not only encapsulated but also that the encapsulated perfume is provided with a deposition aid to increase the efficiency of perfume deposition and retention on fabrics. The deposition aid is preferably attached to the encapsulate by means of a covalent bond, entanglement or strong adsorption, preferably by a covalent bond or entanglement.

10 **Shading dyes**

Shading dye can be used to improve the performance of the compositions. Preferred dyes are violet or blue. It is believed that the deposition on fabrics of a low level of a dye of these shades, masks yellowing of fabrics. A further advantage of shading dyes is that they can be used to mask any yellow tint in the composition itself.

15

Suitable and preferred classes of dyes are discussed below.

Direct Dyes:

Direct dyes (otherwise known as substantive dyes) are the class of water soluble dyes which have an affinity for fibres and are taken up directly. Direct violet and direct blue dyes are preferred.

20

Preferably bis-azo or tris-azo dyes are used.

Preferred dyes are direct violet 7, direct violet 9, direct violet 11, direct violet 26, direct violet 31, direct violet 35, direct violet 40, direct violet 41, direct violet 51, and direct violet 99. Bis-azo copper containing dyes for example direct violet 66 may be used. The benzidine based dyes are less preferred.

25

Preferably the direct dye is present at 0.000001 to 1 wt.% more preferably 0.00001 wt.% to 0.0010 wt.% of the composition.

30

In another embodiment the direct dye may be covalently linked to the photo-bleach, for example as described in WO 2006/024612.

35

Acid dyes:

Cotton substantive acid dyes give benefits to cotton containing garments. Preferred dyes and mixes of dyes are blue or violet. Preferred acid dyes are azine dyes and non-azine dyes. Preferred azine dyes are: acid blue 98, acid violet 50, and acid blue 59, more preferably acid violet 50 and acid blue 98. Other preferred non-azine acid dyes are acid violet 17, acid black 1 and acid blue 29.

Preferably the acid dye is present at 0.0005 wt.% to 0.01 wt.% of the formulation.

10 *Hydrophobic dyes:*

The composition may comprise one or more hydrophobic dyes selected from benzodifuranes, methine, triphenylmethanes, naphthalimides, pyrazole, naphthoquinone, anthraquinone and mono-azo or di-azo dye chromophores. Hydrophobic dyes are dyes which do not contain any charged water solubilising group. Hydrophobic dyes may be selected from the groups of disperse and solvent dyes. Blue and violet anthraquinone and mono-azo dye are preferred.

Preferred dyes include solvent violet 13, disperse violet 27 disperse violet 26, disperse violet 28, disperse violet 63 and disperse violet 77.

20

Preferably the hydrophobic dye is present at 0.0001 wt.% to 0.005 wt.% of the formulation.

Basic dyes:

25 Basic dyes are organic dyes which carry a net positive charge. They deposit onto cotton. They are of particular utility for used in composition that contain predominantly cationic surfactants. Dyes may be selected from the basic violet and basic blue dyes listed in the Colour Index International.

30 Preferred examples include triarylmethane basic dyes, methane basic dye, anthraquinone basic dyes, basic blue 16, basic blue 65, basic blue 66, basic blue 67, basic blue 71, basic blue 159, basic violet 19, basic violet 35, basic violet 38, basic violet 48; basic blue 3, basic blue 75, basic blue 95, basic blue 122, basic blue 124, basic blue 141.

35

Reactive dyes:

Reactive dyes are dyes which contain an organic group capable of reacting with cellulose and linking the dye to cellulose with a covalent bond. They deposit onto cotton.

- 5 Preferably the reactive group is hydrolysed or reactive group of the dyes has been reacted with an organic species for example a polymer, so as to the link the dye to this species. Dyes may be selected from the reactive violet and reactive blue dyes listed in the Colour Index International.
- 10 Preferred examples include reactive blue 19, reactive blue 163, reactive blue 182 and reactive blue, reactive blue 96.

Dye conjugates:

- Dye conjugates are formed by binding direct, acid or basic dyes to polymers or particles
15 via physical forces. Dependent on the choice of polymer or particle they deposit on cotton or synthetics. A description is given in WO 2006/055787.

- Particularly preferred dyes are: direct violet 7, direct violet 9, direct violet 11, direct violet 26, direct violet 31, direct violet 35, direct violet 40, direct violet 41, direct violet 51, direct
20 violet 99, acid blue 98, acid violet 50, acid blue 59, acid violet 17, acid black 1, acid blue 29, solvent violet 13, disperse violet 27 disperse violet 26, disperse violet 28, disperse violet 63, disperse violet 77 and mixtures thereof.

- Shading dye can be used in the absence of fluorescer, but it is especially preferred to use
25 a shading dye in combination with a fluorescer, for example in order to reduce yellowing due to chemical changes in adsorbed fluorescer.

Builders

- The detergent compositions may also optionally contain relatively low levels of organic
30 detergent builder material. Examples include citrates, succinates, malonates, carboxymethyl succinates, carboxylates, polycarboxylates and polyacetyl carboxylates.

- Other suitable organic builders include the higher molecular weight polymers and copolymers known to have builder properties. For example, such materials include
35 appropriate polyacrylic acid, polymaleic acid, and polyacrylic/polymaleic acid copolymers and their salts, for example those sold by BASF under the name SOKALAN™.

If utilized, the organic builder materials may comprise from about 0.5 to 20 wt.%, preferably from 1 to 10 wt.%, of the composition. The preferred builder level is less than 10 wt.% and preferably less than 5 wt.% of the composition.

5 **External Structurants**

The compositions may have their rheology modified by use of a material or materials that form a structuring network within the composition. Suitable structurants include polymers, hydrogenated castor oil, microfibrinous cellulose and natural based structurants for example citrus pulp fibre. Citrus pulp fibre is particularly preferred especially if lipase
10 enzyme is included in the composition.

Visual Cues

The compositions may comprise visual cues of solid material that is not dissolved in the composition. Preferred visual cues are lamellar cues formed from polymer film and
15 possibly comprising functional ingredients that may not be as stable if exposed to the alkaline liquid. Enzymes and bleach catalysts are examples of such ingredients. Also perfume, particularly microencapsulated perfume.

Packaging and dosing

20 Preferably the liquids are 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.

The invention will now be further described with reference to the following non-limiting
25 examples.

Examples

30 The following liquid formulations in table 1 were prepared. The base liquid ingredients were mixed together, and then the post-dosed ingredients added upon cooling to 30°C. formulations A and B are comparative, formulations 1-3 are according to the invention.

Table 1

	A Wt. %	B Wt. %	1 Wt. %	2 Wt. %	3 Wt. %
Demin water (balancing agent)	To 100	To 100	To 100	To 100	To 100
Fluorescer	0.12	0.12	0.12	0.12	0.12
MPG	2.00	-	2.00	-	2.00
Neodol 25-7	3.92	3.92	3.92	3.92	3.92
Thickening polymer (HASE)	1.00	1.00	1.00	1.00	1.00
Monoethanolamine	0.53	1.06	-	-	0.11
Triethanolamine	5.19	6.75	6.75	6.75	6.56
LAS Acid	5.23	3.45	5.28	5.28	5.28
Prifac 5908 fatty acid	1.63	1.63	1.63	1.63	1.63
Dequest 2010	0.70	0.60	0.70	0.60	0.70
SLES 3EO	3.92	3.92	3.92	3.92	3.92
EPEI	1.40	1.40	1.40	1.40	1.40
Soil release polyester polymer	0.47	0.37	0.47	0.37	0.47
Neolone 950	0.01	0.01	0.01	0.01	0.01
Proxel GXL	0.02	0.02	0.02	0.02	0.02
Preservative	0.25	0.25	0.25	0.25	0.25
Post dosed					
Enzymes	1.21	0.92	1.21	0.92	1.21
Perfume	0.65	0.65	0.65	0.65	0.65
Colourants	0.01	0.01	0.01	0.01	0.01
Ratio of TEA:MEA	9.8:1	3.25:1	100% TEA	100% TEA	48:1

- 5 The formulations were made and stored in 100ml bottles at 50°C, and the colour checked by visual appraisal after 2, 3 and 4 weeks.

It was found that formulations A and B were discoloured (showed signs of yellowing) after 2, 3 and weeks. Formulations 1-3 according to the invention did not show any signs of

10 yellowing.

CLAIMS

1. An aqueous laundry liquid detergent composition comprising:-
 - a) from 4 to 50 wt.% of one or more surfactants;
 - 5 b) from 0.1 to 5 wt.%, preferably from 0.25 wt.% to 4 wt.%, more preferably from 0.5 to 2.5 wt.%, of one or more sequestrants, said sequestrants are phosphonic acids and/or salts thereof;
 - c) from 1 to 20 wt.%, preferably from 2 to 18 wt.%, more preferably from 4 to 16 wt.% of triethanolamine;
 - 10 d) from 35 to 94 wt.% of water;wherein if the composition comprises sulfites, they are present at a level of less than 0.1 wt.%, preferably less than 0.01 wt.%, more preferably less than 0.001 wt.%; and, wherein if other alkanolamines are present, then the weight ratio of triethanolamine to the sum of other alkanolamines is greater than 12:1 and
15 wherein the composition comprises from 0.0001 to 1 wt.%, preferably from 0.001 to 0.5 wt.%, more preferably from 0.001 to 0.25 wt.% of an isothiazolinone preservative.
2. A composition according to claim 1 wherein if other alkanolamines are present, then
20 the weight ratio of triethanolamine to the sum of other alkanolamines is greater than 16:1, preferably at least than 20:1, more preferably triethanolamine is the sole alkanolamine present, and most preferably triethanolamine is the sole neutralising species present in the formulation.
- 25 3. A composition according to claim 1 or claim 2, wherein the composition is free from sulfites.
4. A composition according to any preceding claim, wherein the sequestrant is
30 selected from the group consisting of the following phosphonic acids and salts thereof: 1-Hydroxyethylidene-1,1-diphosphonic acid (HEDP); Diethylenetriaminepenta(methylenephosphonic acid) (DTPMP); Hexamethylenediaminetetra(methylenephosphonic acid) (HDTMP); Aminotris(methylenephosphonic acid) (ATMP); Ethylenediaminetetra(methylenephosphonic acid) (EDTMP);

Tetramethylenediaminetetra(methylenephosphonic acid) (TDTMP); and,
Phosphonobutanetricarboxylic acid (PBTC).

5. A composition according to claim 4, wherein the sequestrant is in acid form.
- 5 6. A composition according to claim 5, wherein the sequestrant is 1-Hydroxyethylidene-1,1-diphosphonic acid (HEDP).
7. A composition according to any preceding claim, wherein the surfactant is present
10 at a level of 5 to 40 wt.%, preferably from 6 to 30 wt.%, and wherein the surfactant comprises the anionic surfactants: linear alkylbenzene sulfonate and sodium lauryl ether sulfate, and a nonionic surfactant: alcohol ethoxylate.
8. A composition according to any preceding claim, wherein the composition
15 comprises from 0.05 to 6 wt.%, preferably from 0.1 to 5 wt.% of one or more polyester soil release polymer(s).
9. A composition according to any preceding claim, wherein the composition
20 comprises from 0.25 to 8 wt.%, preferably from 0.5 to 6 wt.% of an alkoxyated polyethyleneimine.
10. A composition according to claim 9, wherein the alkoxyated polyethyleneimine is an ethoxylated polyethyleneimine.
- 25 11. A composition according to any preceding claim, wherein the isothiazolinone is benzisothiazolinone and/or methylisothiazolinone.
12. An aqueous laundry liquid detergent composition according to claim 1 comprising:-
30 a) from 6 to 30 wt.% of a surfactant system comprising linear alkylbenzene sulfonate, sodium lauryl ether sulfate, and alcohol ethoxylate;
b) from 0.5 to 2.5 wt.% of 1-Hydroxyethylidene-1,1-diphosphonic acid (HEDP);
c) from 5 to 16 wt.% of triethanolamine;
d) from 25 to 94 wt.% of water;
e) from 0.5 to 6 wt.% of an ethoxylated polyethyleneimine;
35 f) from 0.1 to 5 wt.% of one or more polyester soil release polymer(s);

g) from 0.001 to 0.25 wt.% of a benzisothiazolinone and/or methylisothiazolinone preservative;

wherein if the composition comprises sulfites, they are present at a level of less than 0.1 wt.%, preferably less than 0.01 wt.%, more preferably less than 0.001 wt.%; and, wherein if other alkanolamines are present, then the weight ratio of triethanolamine to the sum of other alkanolamines is greater than 12:1.

13. A composition according to any preceding claim, further comprising one of more hydrophobically modified alkali swellable emulsion (HASE) copolymers, which may be linear in nature or crosslinked.

14. A composition according to any preceding claim, further comprising one of more of the following ingredients: structurants, foam boosting agents, bactericides, pH buffering agents, polyelectrolytes, anti-shrinking agents, anti-wrinkle agents, anti-oxidants, sunscreens, anti-corrosion agents, drape imparting agents, anti-static agents, ironing aids, colorants, pearlisers, opacifiers, and shading dye.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/062562

A. CLASSIFICATION OF SUBJECT MATTER
INV. C11D3/30 C11D3/36 C11D3/48
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2012/052306 A1 (UNILEVER PLC [GB]; UNILEVER NV [NL]; UNILEVER HINDUSTAN [IN]; BAKER MI) 26 April 2012 (2012-04-26) examples 10,13	1-14

X	WO 2012/104159 A1 (UNILEVER PLC [GB]; UNILEVER NV [NL]; UNILEVER HINDUSTAN [IN]; CARSWELL) 9 August 2012 (2012-08-09) example 9	1-14

	-/--	



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

9 August 2017

Date of mailing of the international search report

18/08/2017

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Culmann, J

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2017/062562

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	HIROYUKI YANO ET AL: "Generation of Maillard-type compounds from triethanolamine alone", JOURNAL OF THE AMERICAN OIL CHEMISTS' SOCIETY (JAOCS), vol. 74, no. 7, 1 July 1997 (1997-07-01), pages 891-893, XP055397619, DE ISSN: 0003-021X, DOI: 10.1007/s11746-997-0234-6 Scheme 1; page 892 -----	1-14

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2017/062562

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2012052306 A1	26-04-2012	CL 2013001087 A1	21-02-2014
		CN 103180423 A	26-06-2013
		EP 2630224 A1	28-08-2013
		ES 2593728 T3	12-12-2016
		WO 2012052306 A1	26-04-2012
		ZA 201302069 B	28-05-2014

WO 2012104159 A1	09-08-2012	AU 2012213597 A1	25-07-2013
		CN 103347928 A	09-10-2013
		EP 2670788 A1	11-12-2013
		ES 2538997 T3	25-06-2015
		WO 2012104159 A1	09-08-2012
		ZA 201305194 B	25-09-2014
