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(54) **METHOD TO PREVENT DISCOLORATION OF COLORED LIQUIDS**

(57) The present invention relates to a method of reducing destruction of colorant dye in a liquid composition in a bottle that is permeable for UV light which method comprises adding organic phosphonic acid compound to said composition.

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Description

[0001] The present application relates to a way for protecting dye-containing liquid compositions, such as textile or hard surface treatment compositions, from discoloration.

[0002] Liquid detergents have traditionally been sold in opaque bottles. However, use of clear (for the present purpose used synonymously with the terms transparent and translucent) bottles can be aesthetically appealing to consumers as they can see the color of the product, its consistency, and suspended particles if they are present.

[0003] However, the use of clear bottles can lead to destruction of colorant by UV light. By UV light is meant light having wavelength of about 250 to about 460 nanometers (nm). Specifically, UVA generally is in range 320-400 nm, UVB about 290 to 320 nm and UVC below 290 nm, down to about 250 nm.

[0004] It has been known in the art that UV absorbers or UV blockers can be added to the bottle material during manufacture of clear bottles to protect them from becoming brittle and to protect the ingredients inside the bottle. Another approach is the addition of UV absorbers or UV blockers to the formulation.

[0005] WO 00/36074 A1 discloses a translucent or transparent aqueous heavy duty liquid in a clear bottle comprising colorant dye and fluorescent dye and/or UV absorber to protect said colorant dye.

[0006] WO 00/43486 A discloses a method for improving dye stability in colored acidic formulations by introducing chelants selected from aminocarboxylates, aminophosphonates or polyfunctionally-substituted aromatic chelants.

[0007] WO 2014/095459 A discloses the use of ethanol in a translucent or transparent aqueous heavy duty liquid for the effective protection of colorants therein against discoloration by UV light.

[0008] The use of known UV absorbers or fluorescent dyes leads not in any event to an effective UV protection for colorant dyes. Additionally, the use of UV absorbers lead to high costs. For this reasons there is a need for an alternative, cost efficient and effective route for UV protection of colorant dyes in translucent or transparent liquids.

[0009] It was found, that especially in acidic media the UV-stability of a colorant dye, especially of a combination of at least one colorant dye and at least one fluorescent dye, is improved by adding at least one organic phosphonic acid compound, having at least two phosphonic acid residues, to said composition.

[0010] Accordingly, it is an object of the present invention to provide a cheap way for stabilizing dye-containing liquid compositions, especially dye-containing liquid textile or hard surface treatment compositions.

[0011] This object is achieved by a method of reducing destruction of colorant dye in a liquid composition (preferably having a pH-value < 7 (at 20°C)) to be stored in a bottle that is permeable for UV light which method comprises adding at least one organic phosphonic acid compound, having at least two phosphonic acid residues to said composition.

[0012] It has now surprisingly been found that the addition of at least one organic phosphonic acid compound, having at least two phosphonic acid residues effectively protects a colored liquid composition against destruction of the colorant dye. Since at least one organic phosphonic acid compound, having at least two phosphonic acid residues is a cheap chemical that is often and widely used, the color stability of dyed liquid compositions can be improved in a simple and cost effective way.

[0013] It is preferred that the liquid composition is a liquid textile or hard surface treatment composition. Liquid textile or hard surface treatment compositions are often intensively dyed and, in addition, are packaged in clear bottles.

[0014] In a preferred embodiment the at least one organic phosphonic acid compound, having at least two phosphonic acid residues is added in an amount of at 0.001 to 1,0 wt.%, , particularly preferred 0,01 to 1,0 wt.%, more preferred 0,01 to 0,5 % by wt.%, most preferred of 0,01 to 0,03 % by wt., of the liquid composition. It has surprisingly been shown that already very little amounts of said organic phosphonic acid compound are sufficient to effectively reduce the destruction of a colorant dye in a liquid composition, especially at pH < 7 (at 20°C).

[0015] Another object of the invention is a liquid aqueous composition having a pH-value < 7 (at 20°C), comprising at least one colorant dye and at least one organic phosphonic acid compound, having at least two phosphonic acid residues.

[0016] Matter (e.g. a compound or a composition) is defined as a liquid, if it is in the liquid state at 20°C, 1013 mbar.

[0017] Matter (e.g. a compound or a composition) is defined as a solid, if it is in the solid state at 20°C, 1013 mbar.

[0018] A chemical compound is defined to be an organic compound, if said compound comprises a covalent bond between carbon and hydrogen. Said definition for example holds for organic phosphonic acid compounds.

[0019] A chemical compound is defined to be an inorganic compound, if said compound does not comprise a covalent bond between carbon and hydrogen.

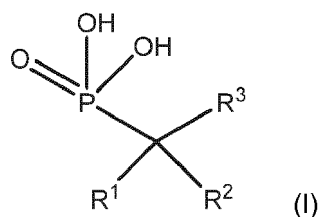
[0020] The pH-value is determined at 20°C. A preferred pH value is pH < 6.5.

"phosphonic acid" includes according to this invention the free acid form of a phosphonic acid group $-P(=O)(OH)_2$ and its neutralized phosphonate form. In the corresponding phosphonate group at least one of the acidic hydrogen atoms of said phosphonic acid group is neutralized, resulting in a negative charge at the respective oxygen atom, whereas said negative charge is electronically neutralized by a counter ion M^+ . A preferred phosphonate form is a sodium salt of said phosphonic acid, in which at least one of said acidic hydrogen atoms is neutralized and the resulting negative charge is electronically neutralized by sodium counter ion. The same definition holds for "sulfonic acid" and its sulfonic acid group $-S(=O)_2(OH)$ *mutatis mutandis*.

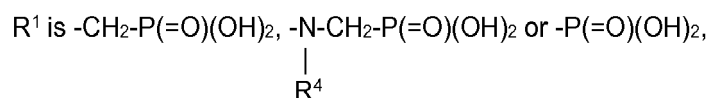
[0021] Substituent means a chemical group comprising at least one atom functioning as a substitute for a hydrogen atom in a given molecule or chemical structure.

"colorant dye" is defined as a dye compound, which dyes the liquid aqueous composition.

[0022] A preferred organic phosphonic acid compound is selected from at least one compound of formula (I)



wherein

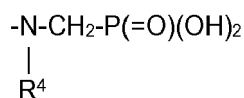


R² is hydrogen or hydroxy,

R³ is hydrogen or methyl,

R⁴ is hydroxyethyl, a linear or branched ethylene imine backbone with at least one -CH₂-P(=O)(OH)₂ group attached to a nitrogen atom, whereas said ethylene imine backbone is composed of 1 to 1000 ethylene imine units.

[0023] In a particularly preferred embodiment, according to formula (I) R² and R³ denote hydrogen and R¹ is a



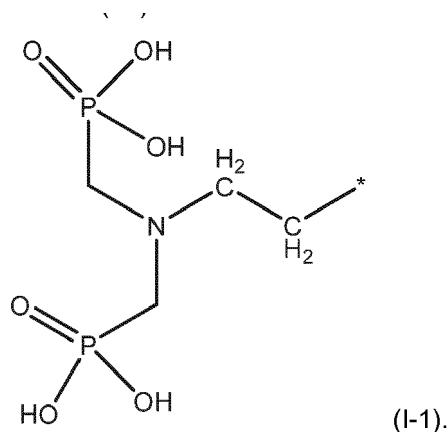
group, wherein R⁴ is a linear or branched ethylene imine backbone with at least one -CH₂-P(=O)(OH)₂ group attached to a nitrogen atom, whereas said ethylene imine backbone is composed of 1 to 1000 ethylene imine units.

[0024] In any event, R⁴ of formula I binds through a carbon atom of said linear or branched ethylene imine backbone, especially the β-carbon atom of an ethylene imine unit.

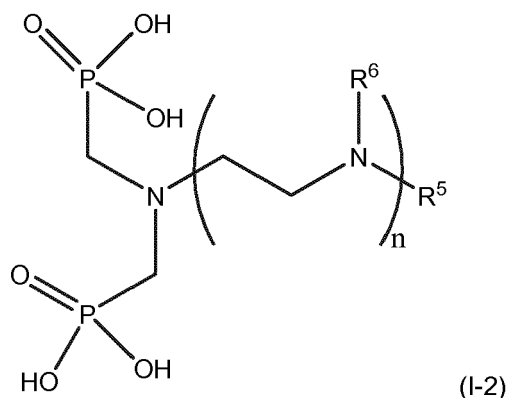
[0025] The ethylene imine backbone of R⁴ is composed out of 1 to 1000 ethylene imine units, which can be linear or branched.

[0026] The linear ethylene imine backbone of R⁴ is terminated by a -NH₂-group, with at least one -CH₂-P(=O)(OH)₂ substituent. If the linear ethylene imine backbone comprises more than one units ethylene imine, at least one -NH-group within the chain bears a -CH₂-P(=O)(OH)₂ substituent.

[0027] It is preferred, that the linear or branched ethylene imine backbone comprises at least one moiety of formula (I-1)



[0028] A particularly preferred organic phosphonic acid compound is selected from at least one compound of formula (I-2)



wherein n is an integer from 1 to 1000, preferred from 1 to 12,
R⁵ and R⁶ independently from each other denote hydrogen or -CH₂-P(=O)(OH)₂.

[0029] In a particularly preferred embodiment, according to formula (I-2) n is an integer from 1 to 5, preferably from 1 to 3, and R⁵ and R⁶ denote -CH₂-P(=O)(OH)₂.

[0030] The branched ethylene imine backbone has ethylene imine grafts. Each ethylene imine graft can be either linear or branched. Every graft of the branched ethylene imine backbone is terminated by a -NH₂-group, whereas at least one NH₂-terminus binds at least one -CH₂-P(=O)(OH)₂ substituent. The branched ethylene imine backbone comprises at least one -NH-group within the chain, whereas at least one of these -NH-group bears a -CH₂-P(=O)(OH)₂ substituent. The branched ethylene oxide comprises at least one tertiary nitrogen atom having a covalent bond to three ethylene imine moieties. Said tertiary nitrogen atom functions as a connection for a branch based on an ethylene imine moiety.

[0031] A most preferred organic phosphonic acid compound is Diethylene triamine penta(methylenephosphonic acid) (CAS number: 15827-60-8; according to Formula (I-2): n = 2, R⁵ and R⁶ denote -CH₂-P(=O)(OH)₂ and/or its phosphonates.

[0032] In a preferred embodiment, the phosphonic acid is comprised in an amount of 0.001 to 0.5 wt.%, particularly preferred in an amount of 0.005 to 0.02 wt.%, related to the weight of the total composition.

[0033] In a preferred embodiment of this invention said liquid composition comprises at most 0.5 wt.%, particularly preferred at most 0.05 wt.%, colorant dye.

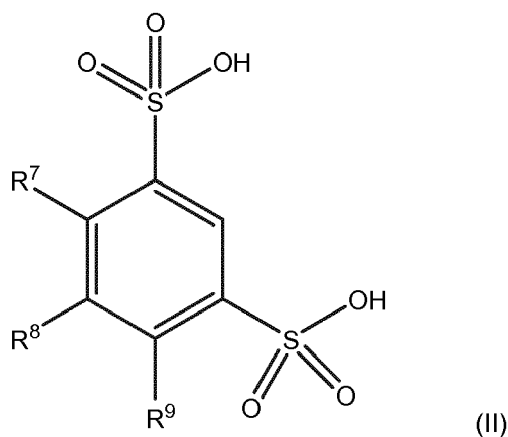
[0034] In a preferred embodiment of this invention, the colorant dye is water soluble (1 wt.% at 20°C in water at pH 5).

[0035] The invention is applicable to any type of colorant dye which may be destroyed by UV light. Non limiting examples of such include, but are not limited to the following: Acid Blue 145, Acid Blue 9, Pigment Green No. 7, Solvent Green 7, Acid Blue 80, Acid Violet 48, Acid Yellow 23, Acid Yellow 17, Acid Red 52, Food Yellow 3, anthraquinone dyes, and xanthene dyes. It is preferred that the colorant dye is selected from red acid dye, xanthene dyes and mixtures thereof.

[0036] The colorant dyes are preferably present in an amount of from 0.0001% to 1% by wt. of the liquid composition and preferably in an amount of from 0.001 to 0.4% by wt. of the composition.

[0037] It is preferred, that the liquid composition comprises as a colorant dye at least one acid dye, comprising at least one anionic group. Particularly preferred are liquid compositions according to this invention, comprising as said colorant dye at least one colorant dye comprising at least one sulfonic acid group.

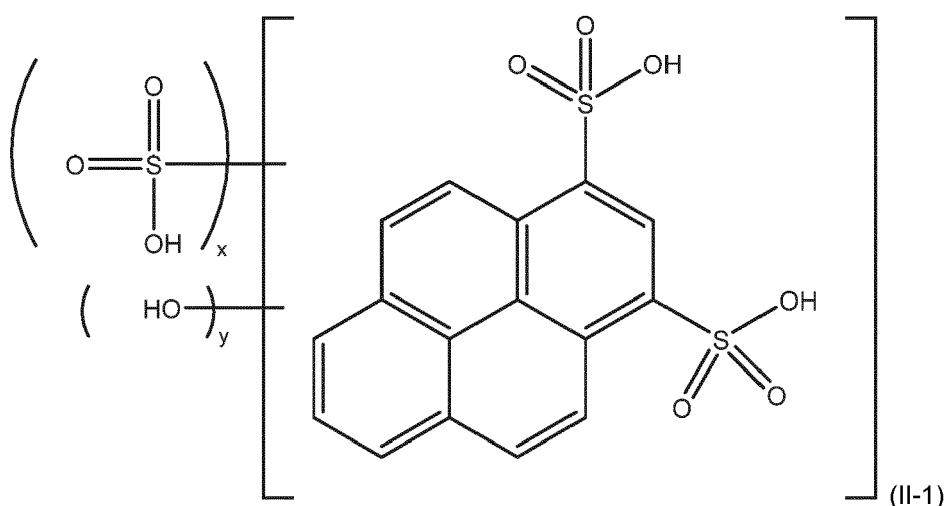
[0038] It is particularly preferred, that the liquid composition comprises as colorant dye at least one dye according to formula (II)



wherein R^7 and R^8 denote independently hydrogen or together form with the benzene moiety a condensed carbocyclic ring system, comprising 1 to 3 six membered rings, which may bear at least one group selected from hydroxy or sulfonic acid residues,

R^9 denotes a xanthylum-9-yl residue, which may bear at least one group selected from methyl, hydroxyl, sulfonic acid, ($\text{C}_1\text{-C}_4$)-dialkylamino residues, or R^9 and R^8 together form with the benzene moiety a condensed carbocyclic ring system, comprising 1 to 3 six membered rings, which may bear at least one group selected from hydroxy or sulfonic acid residues.

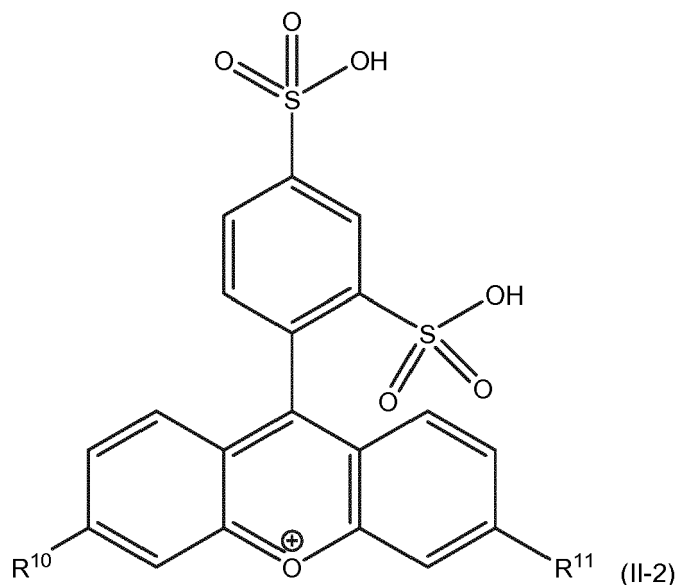
[0039] A particularly preferred colorant dye is selected from at least one compound of formula (II-1)



wherein x and y independently are an integer from 1 to 3.

[0040] A particularly preferred colorant dye of formula (II) and (II-1) is 8-hydroxypyrene-1,3,6-trisulfonicacid (CAS number: 6358-69-6).

[0041] A particularly preferred colorant dye is selected from at least one compound of formula (II-2)



wherein R^{10} and R^{11} denote independently hydroxyl or N,N-di(C_1 - C_4)-alkylamino.

[0042] It is most preferred, that the liquid composition comprises at least one colorant of formula (II-1) and at least a second acid dye, comprising at least one anionic group. Said second acid dye is according to another embodiment preferably selected from at least one colorant dye of formula (II-2).

[0043] In a preferred embodiment the liquid composition is a transparent or translucent liquid composition since stabilization against discoloration/color change is especially necessary in this case.

[0044] The invention is described in greater detail below on the basis of examples, among other things.

[0045] The liquid composition is an aqueous liquid composition and preferably contains water as main solvent. In a preferred embodiment the liquid composition is an aqueous liquid textile or hard surface treatment composition.

[0046] In addition to the organic phosphonic acid and the colorant dye, a liquid composition may contain further ingredients that further improve the applications-engineering or aesthetic properties of the liquid composition.

[0047] In the context of the present invention, a liquid composition by preference additionally contains one or more substances from the group of surfactants, builder, enzymes, non-aqueous solvents, perfume, thickeners, pH adjusting agents, fluorescing agents, hydrotopes, silicone oils, anti-redeposition agents, anti-gray agents, shrinkage preventers, wrinkle protection agents, dye transfer inhibitors, corrosion inhibitors, antistatic agents, bittering agents, ironing adjuvants, electrolytes, proofing and impregnation agents, swelling and anti-slip agents, softening compounds, biocidal compounds and UV absorbers.

[0048] From the above mentioned further ingredients surfactants, enzymes, non-aqueous solvents, perfume, pH adjusting agents, fluorescing agents, silicone oils, soil-release polymers, anti-gray agents, dye transfer inhibitors, electrolytes and bittering agents are most preferred included into a liquid textile or hard surface treatment composition.

[0049] The compositions of the invention preferably additionally contain one or more surfactants selected from the group consisting of anionic, nonionic, cationic, amphoteric and zwitterionic surfactants and mixtures thereof. The preferred surfactants for use in the liquid aqueous composition is at least one cationic surfactant, mixtures of at least one cationic surfactants and at least one nonionic surfactant although it is to be understood that any surfactant may be used alone or in combination with any other surfactant or surfactants.

[0050] The liquid composition preferably comprises in addition to at least one colorant dye and to at least one organic phosphonic acid compound, having at least two phosphonic acid residues, at least one cationic surfactant. The cationic surfactant may be present in the composition in a quantity of 0.1 wt.% to 1.0 wt.%, preferably 0.2 wt.% to 0.7 wt.%, more preferably 0.25 wt.% to 0.6 wt.% and most preferably 0.25 to 0.35 wt.%. It is particularly preferred from a toxicological and ecological viewpoint for the quantity of cationic surfactant compound to be less than 2.5 wt.%.

[0051] In a preferred embodiment the cationic surfactant is a quaternary ammonium compound.

[0052] Suitable quaternary ammonium compounds (QACs) have the general formula $(R^{15})(R^{12})(R^{13})(R^{14})N^+X^-$, wherein each of R^{12} , R^{13} , R^{14} and R^{15} is independently linear or branched C_1 - C_{22} alkyl, C_2 - C_{22} alkenyl, C_2 - C_{22} alkynyl or C_7 - C_{28} alk(en)ylaryl that can optionally be substituted or any two or three of R^{12} , R^{13} , R^{14} and R^{15} combine to form a 5-6-membered, optionally aromatic, heterocyclic ring with the nitrogen atom to which they are attached; and X^- is an anion.

[0053] The alkyl moieties can comprise 1 to 22 carbon atoms, but preferably are either lower alkyl, comprising 1 to 4 carbon atoms, or C_8 - C_{18} alkyl. They are preferably linear. When substituted they can be substituted with any one or more substituents selected from the group consisting of -OR, halo, nitro, -NRR', cyano, -C(O)R, -C(O)OR, -(CO)NRR',

-NR'C(O)R, -OC(O)R, C₅-C₂₀ aryl, C₃-C₂₀ cycloalk(en)yl, 3- to 8-membered heterocycloalk(en)yl, and 5- to 20-membered heteroaryl, wherein R and R' are independently selected from H, C₁-C₁₀ alkyl, C₂-C₁₀ alkenyl, C₂-C₁₀ alkynyl, C₅-C₁₄ aryl, C₃-C₈ cycloalk(en)yl, 5- to 14- membered heteroaryl, comprising 1 to 4 heteroatoms selected from N, O, and S, and 5- to 14- membered heterocycloalk(en)yl, comprising 1 to 4 heteroatoms selected from N, O, and S.

[0054] The alkenyl and alkynyl moieties comprise one or more carbon-carbon double bonds or triple bonds, respectively, and are otherwise defined as alkyl above. Specifically, they are preferably linear and if substituted they are substituted with a substituent selected from the above list of substituents.

[0055] Cycloalkyl refers to a non-aromatic carbocyclic moiety, such as cyclopentanyl, cyclohexanyl and the like. Cycloalkenyl refers to non-aromatic carbocyclic compounds that comprise at least one C-C double bond. Similarly, heterocycloalk(en)yl relates to cycloalk(en)yl groups wherein 1 or more ring carbon atoms are replaced by heteroatoms, preferably selected from N, O and S.

[0056] Aryl relates to an aromatic ring that is preferably monocyclic or consists of condensed aromatic rings. Preferred aryl substituents are C₆-C₁₂ aryl moieties, such as phenyl, naphthyl, anthracenyl and phenanthrenyl.

[0057] Heteroaryl refers to aromatic moieties that correspond to the respective aryl moiety wherein one or more ring carbon atoms have been replaced by heteroatoms, such as N, O and S.

[0058] Alkylaryl and alkenylaryl relate to alkyl or alkenyl groups that are substituted with an aryl group, such as benzyl.

[0059] In preferred embodiments of the invention R¹² and R¹³ are unsubstituted C₁-C₄ alkyl, preferably methyl, and/or R¹⁴ and R¹⁵ are defined as follows:

(i) R¹⁴ is (C₁-C₄)alkyl(C₆-C₁₄)aryl, preferably benzyl, and R¹⁵ is unsubstituted C₈-C₁₈ alkyl; or (ii) R¹⁴ is unsubstituted C₁-C₄ alkyl, preferably methyl, and R¹⁵ is (meth)acryloxy(C₁-C₄)alkyl, preferably acryloxyethyl; or (iii) R¹⁴ and R¹⁵ are independently unsubstituted C₈-C₁₈ alkyl.

[0060] In case any two or three of R¹²-R¹⁵ combine to form a cyclic moiety with the nitrogen atom to which they are attached, this means that for example two or three of R¹²-R¹⁵ together are an alkyl or alkenyl group as defined above that forms a ring with the nitrogen atom. The ring may be an aromatic, monocyclic or bicyclic ring.

[0061] In various embodiments of the invention, X⁻ is selected from the group consisting of halide, sulfate, hydroxide, phosphate, preferably halide, more preferably chloride. Halide includes fluoride, chloride, bromide and iodide. The anion can be selected such that the QAC is render water-soluble. In specific embodiments, the anion is selected from halide, methosulfate, methophosphate or phosphate and mixtures of these or similar anions. Alternatively, the anion may be a carboxylic acid derived organic anion such as acetate, propionate, citrate, lactate, tartrate and the like

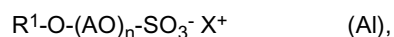
[0062] QACs can be produced by reacting tertiary amines with alkylating agents, such as e.g. methyl chloride, benzyl chloride, dimethyl sulfate, dodecyl bromide, but also ethylene oxide. The alkylation of tertiary amines with a long alkyl residue and two methyl groups is achieved particularly readily, and even the quaternization of tertiary amines with two long residues and a methyl group can be carried out under mild conditions with the aid of methyl chloride. Amines having three long alkyl residues or hydroxy-substituted alkyl residues are of low reactivity and are preferably quaternized with dimethyl sulfate.

[0063] Suitable QACs are for example benzalkonium chloride (N-alkyl-N,N-dimethylbenzylammonium chloride, CAS No. 8001-54-5), benzalkon B (*m,p*-dichlorobenzyltrimethyl-C₁₂-alkylammonium chloride, CAS No. 58390-78-6), benzoxonium chloride (benzyltrimethylammonium chloride), cetyltrimonium bromide (N-hexadecyl-N,N,N-trimethylammonium bromide, CAS No. 57-09-0), benzethonium chloride (N,N-dimethyl-N-[2-[2-[p-(1,1,3,3-tetramethylbutyl)phenoxy]ethoxy]ethyl]benzylammonium chloride, CAS No. 121-54-0), dialkyldimethylammonium chlorides such as di-*n*-decyldimethyl-ammonium chloride (CAS No. 7173-51-5-5), didecyldimethylammonium bromide (CAS No. 2390-68-3), dioctyldimethylammonium chloride, 1-cetylpyridinium chloride (CAS No. 123-03-5) and thiazoline iodide (CAS No. 15764-48-1) and mixtures thereof. Particularly preferred QACs are dialkyldimethylammonium chlorides, in particular di-*n*-decyldimethylammonium chloride, N-octadecyl-N,N,N-trimethylammonium chloride, N-hexadecyl-N,N,N-trimethylammonium chloride and the benzalkonium chlorides with C₈-C₁₈ alkyl residues, in particular C₁₂-C₁₄alkylbenzyltrimethylammonium chloride. Another preferred compound is methyl-N-(2-hydroxyethyl)-N,N-di(caproyloxyethyl)ammonium methosulfate.

[0064] The dialkyldimethylammonium halides, the benzalkonium halides and/or substituted benzalkonium halides are commercially available, for example as Barquat® from Lonza, Marquat® from Mason, Variquat® from Evonik Industries and Hyamine® from Lonza.

[0065] It is possible that the liquid composition comprises an anionic surfactant. Anionic surfactants are ingredients of liquid treatment compositions because of their cleansing and emulsifying properties. Anionic surfactants are particularly good at keeping the dirt away from textile and hard surfaces, and removing oily soil residues from textile and hard surfaces.

[0066] For example, said liquid compositions may contain a surfactant of the following general formula AI:



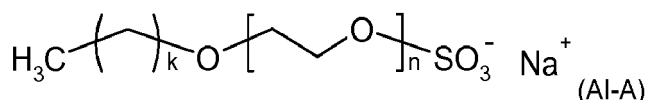
wherein

R^1 is linear or branched, saturated or unsaturated, substituted or un-substituted hydrocarbon wherein the total number of carbon atoms is from 1 to 24;
 AO is an ethylene oxide- (EO) or propylene oxide- (PO) group;
 n is an integer from 1 to 50;
 X is a monovalent metal cation, the n-th part of an n-valent metal cation, an ammonium cation or a substituted ammonium cation.

[0067] In formula (AI) R^1 is a linear or branched, substituted or unsubstituted alkyl-, aryl- or alkylaryl group, preferably a linear, unsubstituted alkyl group, more preferably a fatty alcohol residue. Preferred residues R^1 are chosen from decyl-, undecyl-, dodecyl-, tridecyl-, tetradecyl-, pentadecyl-, hexadecyl-, heptadecyl-, octadecyl-, nonadecyl-, eicosyl residues and their mixtures, wherein the residues with an even number of carbon atoms are preferred. Particularly preferred residues R^1 are derived from C_{12} - C_{18} -fatty alcohols, for example from coconut fatty alcohol, tallow fatty alcohol, lauryl-, myristyl-, cetyl- or stearyl alcohol or from C_{10} - C_{20} -oxo alcohols.

[0068] AO is an ethylene oxide (EO) or propylene oxide (PO) group, preferably an ethylene oxide group. The index n is an integral number from 1 to 50, preferably from 1 to 20 and most preferably from 2 to 10. Particularly preferred, n is 2, 3, 4, 5, 6, 7 or 8. X is a monovalent cation or the n-th part of an n-valent cation, preferred cations are alkali metal ions, especially Na^+ or K^+ , wherein Na^+ is particularly preferred. Further cations X^+ can be chosen from NH_4^+ , $\frac{1}{2} Zn^{2+}$, $\frac{1}{2} Mg^{2+}$, $\frac{1}{2} Ca^{2+}$, $\frac{1}{2} Mn^{2+}$, and their mixtures.

[0069] Particularly preferred surfactants of formula (AI) are chosen from fatty alcohol ether sulphates of formula I-A



with $k = 11$ to 19 , $n = 2, 3, 4, 5, 6, 7$ or 8 . Most preferred representatives of this formula are Na - C_{12-14} fatty alcohol ether sulphates with 2 EO ($k = 11-13$, $n = 3$ in formula I-A).

[0070] Other suitable anionic surfactants can be preferably chosen from fatty alcohol sulphates and/or alkyl benzene sulfonates. Accordingly, liquid textile or hard surface treatment compositions may contain a surfactant of the following general formula All:



wherein

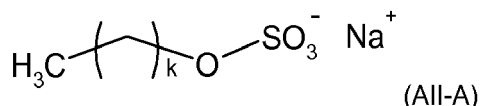
R^3 is linear or branched, saturated or unsaturated, substituted or un-substituted hydrocarbon wherein the total number of carbon atoms is from 1 to 24;
 A is -O- or a chemical bond;
 Y is a monovalent metal cation, the n-th part of an n-valent metal cation, an ammonium cation or a substituted ammonium cation.

[0071] In formula (All) R^3 is a linear or branched, substituted or unsubstituted alkyl-, aryl- or alkylaryl group, preferably a linear, unsubstituted alkyl group, more preferably a fatty alcohol residue. Preferred residues R^1 are chosen from decyl-, undecyl-, dodecyl-, tridecyl-, tetradecyl-, pentadecyl-, hexadecyl-, heptadecyl-, octadecyl-, nonadecyl-, eicosyl residues and their mixtures, wherein the residues with an even number of carbon atoms are preferred. Particularly preferred residues R^1 are derived from C_{12} - C_{18} -fatty alcohols, for example from coconut fatty alcohol, tallow fatty alcohol, lauryl-, myristyl-, cetyl- or stearyl alcohol or from C_{10} - C_{20} -oxo alcohols.

[0072] A is -O- or a chemical bond. X is a monovalent cation or the n-th part of an n-valent cation, preferred cations are alkali metal ions, especially Na^+ or K^+ , wherein Na^+ is particularly preferred. Further cations X^+ can be chosen from NH_4^+ , $\frac{1}{2} Zn^{2+}$, $\frac{1}{2} Mg^{2+}$, $\frac{1}{2} Ca^{2+}$, $\frac{1}{2} Mn^{2+}$, and their mixtures.

[0073] Depending on whether A is a bridging oxygen or a chemical bond, formula (All) describes sulphate surfactants or sulfonate surfactants.

[0074] Particularly preferred surfactants of formula (All) are chosen from fatty alcohol sulphates of formula (All-A)

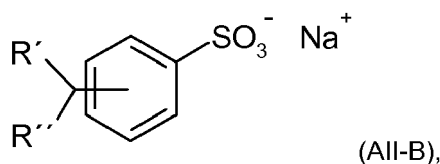


with $k = 11$ to 19 . Most preferred representatives of this formula are Na-C_{12-14} fatty alcohol sulphates ($k = 11-13$ in formula All-A).

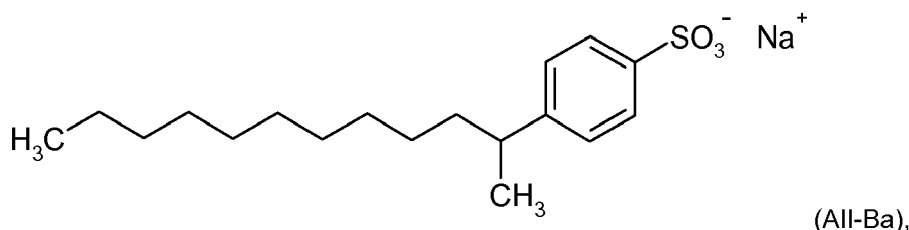
[0075] Even more preferred surfactants of formula (All) are sulfonate surfactants ($A = \text{chemical bond}$). Here, R^3 preferably is a linear or branched unsubstituted alkylaryl residue.

[0076] X is a monovalent cation or the n -th part of an n -valent cation, preferred cations are alkali metal ions, especially Na^+ or K^+ , wherein Na^+ is particularly preferred. Further cations X^+ can be chosen from NH_4^+ , $\frac{1}{2} \text{Zn}^{2+}$, $\frac{1}{2} \text{Mg}^{2+}$, $\frac{1}{2} \text{Ca}^{2+}$, $\frac{1}{2} \text{Mn}^{2+}$, and their mixtures.

[0077] Such most preferred surfactants are chosen from linear or branched alkyl benzene sulfonates of formula All-B



in which R' and R'' together have 9 to 19, preferably 11 to 15 and most preferably 11 to 13 C-atoms. A particularly preferred representative of this formula can be described by formula All-Ba:



[0078] It is preferred that the anionic surfactant is present at a level of from 1 % up to 20 % by weight of said composition and, preferably, at a level of from 2 % up to 15 % by weight of said composition.

[0079] The liquid composition may also contain a non-ionic surfactant as additional ingredient at a level up to 5 % by weight of the liquid textile or hard surface treatment composition.

[0080] The nonionic surfactant that can be used are by preference alkoxylated, advantageously ethoxylated, in particular primary alcohols having by preference 8 to 18 carbon atoms and an average of 1 to 12 mol ethylene oxide (EO) per mol of alcohol, in which the alcohol residue can be linear or preferably methyl-branched in the 2-position, or can contain mixed linear and methyl-branched residues, such as those that are usually present in oxo alcohol residues. Particularly preferred, however, are alcohol ethoxylates having linear residues made up of alcohols of natural origin having 12 to 18 carbon atoms, e.g. from coconut, palm, tallow, or oleyl alcohol, and an average of 2 to 8 EO per mol of alcohol. The preferred ethoxylated alcohols include, for example, C_{12-14} alcohols with 3 EO, 4 EO, 5 EO, or 7 EO, C_{9-11} alcohols with 7 EO, C_{13-15} alcohols with 3 EO, 5 EO, 7 EO, or 8 EO, C_{12-18} alcohols with 3 EO, 5 EO, or 7 EO, and mixtures thereof, such as mixtures of C_{12-14} alcohol with 3 EO and C_{12-18} alcohol with 7 EO. The degrees of ethoxylation indicated represent statistical averages, which can correspond to an integral or a fractional number for a specific product. Preferred alcohol ethoxylates exhibit a restricted distribution of homologs (narrow range ethoxylates, NRE). In addition to these non-ionic active detergent species, fatty alcohols with more than 12 EO can also be used. Examples of these are tallow fatty alcohol with 14 EO, 25 EO, 30 EO, or 40 EO. Nonionic active detergent species that contain EO and PO groups together in the molecule are also usable according to the present invention. Block copolymers having EO-PO block units or PO-EO block units, but also EO-PO-EO copolymers or PO-EO-PO copolymers, can be used in this context. Also usable, of course, are mixed alkoxylated nonionic active detergent species in which EO and PO units are distributed statistically rather than in block fashion. Such products are obtainable by the simultaneous action of ethylene oxide and propylene oxide on fatty alcohols. These non-ionic surfactants are obtainable, for example, under the commercial name Dehydol® (from Cognis).

[0081] Ampholytic surfactants can be broadly described as derivatives of aliphatic or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical may be a straight chain or a branched and wherein one of

the aliphatic substituents contains from 8 to 18 carbon atoms and at least one contains an anionic water-solubilizing group, e.g. carboxy, sulfonate, sulfate. A preferred ampholytic surfactant is cocamidopropyl betaine.

[0082] Preferably, the textile or hard surface treatment composition additionally contains a perfume composition in order to impart a pleasant scent to the laundry treated therewith and to the textile or hard surface treatment composition itself.

[0083] In a preferred embodiment, the liquid textile or hard surface treatment composition contains a perfume composition in a quantity of usually up to 3 wt.%, preferably 0.05 to 2 wt.%, particularly 0.1 to 1.5 wt.% and particularly preferably 0.2 to 1 wt.%, in each case based on the total liquid textile or hard surface treatment composition.

[0084] The perfume composition can contain individual fragrance compounds, for example the synthetic products of the type of the esters, ethers, aldehydes, ketones, alcohols and hydrocarbons. Preferably, however, mixtures of various fragrances are used which together produce an attractive scent. The perfume composition can also contain natural fragrance compounds as may be obtained from plant sources. The perfume composition of the textile or hard surface treatment composition can also contain at least one aromatherapy component such as an essential oil. In another preferred embodiment, the fabric washing liquid composition comprises an encapsulated perfume and a free perfume. The use of pro-fragrances in the perfume composition may be also advantageous.

[0085] The treatment compositions can be used to clean hard surfaces or textile fabrics. For the purposes of the present invention, hard surfaces for example comprise surfaces of stone or ceramic materials, rigid plastics materials, glass, porcelain or metal. Hard surfaces may be, for example, tableware, walls, tiles, work surfaces, painted surfaces, flooring or sanitary articles.

[0086] The textile or hard surface treatment composition is manufactured using usual and known methods and processes. For example, the constituents of the textile or hard surface treatment composition can be simply mixed in agitator vessels, the water, organic phosphonic acid compound and optional additional actives usefully being prepared first. After cooling under stirring (if necessary at all, the further constituents are then added in portions and) the pH is adjusted.

Examples

[0087] The following compositions according to table 1 were prepared by mixing the components in water and adjusting the final pH value with citric acid. All amounts given in table 1 are wt.% if not otherwise noted.

Table 1:

ingredient	V1	E1
BAC 50® ¹	1,20	1,20
genaminox LA ²	1,70	1,70
acusol OP 305 ³	3,00	3,00
diethylene triamine penta(methylenephosphonic acid)	-	0,1
solvent Green 7	0,0003	0,0003
acid Red 52	0,0014	0,0014
isopropanol	0,50	0,50
perfume	0,60	0,60
citric acid	ad pH 5.5	ad pH 5.5
water	ad 100	ad 100
¹ cocoalkyl dimethyl benzyl ammonium chloride (50 wt.% active matter in water) (Thor)		
² C ₁₂₋₁₄ -alkyl dimethyl amine oxide (30 wt.% active matter) (Clariant)		
³ Acrylates/PEG-10 maleate/styrene copolymer (40 wt.% active matter) (Rohm & Haas)		

[0088] When subjected to UV light (the lamp spectrum corresponded to natural sunlight) for 72 and 144 hours E1 showed no or only little change in color. In contrast, identical liquid compositions but without organic phosphonic acid showed after 72 and 144 hours exposure to UV light a substantial color fading and/or discoloration. All liquid compositions were opaque.

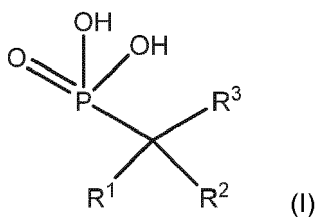
Table 2: EP color values

Product	L*	a*	b*
Initial			
E1	39.5	34.3	-16.3
V1	39.3	34.3	-16.4
After UV exposure 72h			
E1	40.9	28.9	-10.0
V1	41.3	25.3	-9.4
After UV exposure 144h			
E1	43.6	23.9	-6.9
V1	45.3	15.0	-2.8

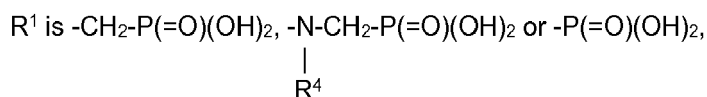
[0089] The data also clearly show that the composition without organic phosphonic acid undergoes a dramatic change in color and that little amounts of organic phosphonic acid significantly reduce the destruction of colorant dye.

Claims

1. Liquid aqueous composition having a pH-value < 7 (at 20°C), comprising at least one colorant dye and at least one organic phosphonic acid compound, having at least two phosphonic acid residues.
2. Liquid aqueous composition according to claim 1, **characterized in that** said organic phosphonic acid compound is selected from at least one compound of formula (I)



wherein

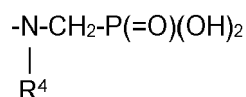


R² is hydrogen or hydroxy,

R³ is hydrogen or methyl,

R⁴ is hydroxyethyl, a linear or branched ethylene imine backbone with at least one -CH₂-P(=O)(OH)₂ group attached to a nitrogen atom, whereas said ethylene imine backbone is composed of 1 to 1000 ethylene imine units.

3. Liquid aqueous composition according to claim 2, **characterized in that** according to formula (I) R² and R³ denote hydrogen and R¹ is a

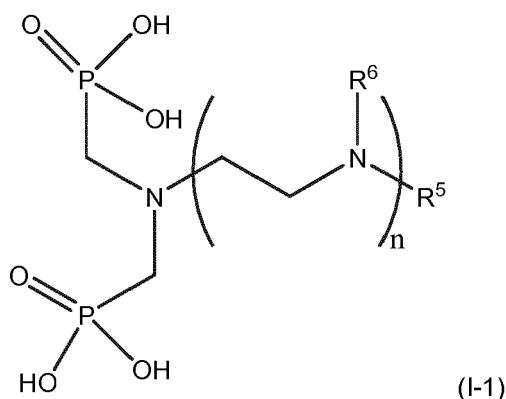


group,

wherein R⁴ is a linear or branched ethylene imine backbone with at least one -CH₂-P(=O)(OH)₂ group attached to

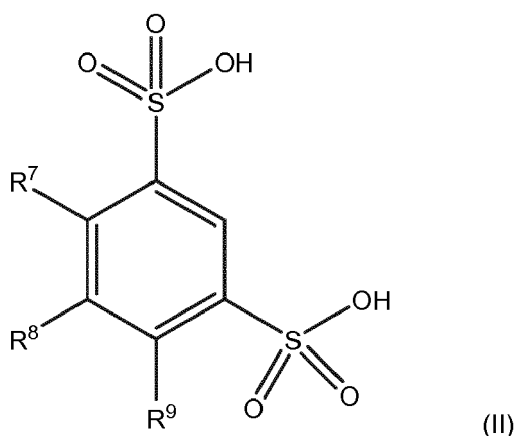
a nitrogen atom, whereas said ethylene imine backbone is composed of 1 to 1000 ethylene imine units.

4. Liquid aqueous composition according to any of the preceding claims, **characterized in that** said organic phosphonic acid compound is selected from at least one compound of formula (I-1)



wherein n is an integer from 1 to 1000, preferred from 1 to 12,
R⁵ and R⁶ independently from each other denote hydrogen or -CH₂-P(=O)(OH)₂.

5. Liquid aqueous composition according to any of the preceding claims, **characterized in that** the phosphonic acid is comprised in an amount of 0.001 to 1,0 wt.%, particularly preferred in an amount of 0.01 to 0.03 wt.%, related to the weight of the total composition.
6. Liquid aqueous composition according to any of the preceding claims, **characterized in that** it comprises at most 0.5 wt.%, particularly preferred at most 0.05 wt.%, colorant dye.
7. Liquid aqueous composition according to any of the preceding claims, **characterized in that** the liquid composition comprises as a colorant dye at least one acid dye, comprising at least one anionic group.
8. Liquid aqueous composition according to any of the preceding claims, **characterized in that** the liquid composition comprises as a colorant dye at least one dye of formula (II)



wherein R⁷ and R⁸ denote independently hydrogen or together form with the benzene moiety a condensed carbocyclic ring system, comprising 1 to 3 six membered rings, which may bear at least one group selected from hydroxy or sulfonic acid residues,

R⁹ denotes a xanthylum-9-yl residue, which may bear at least one group selected from methyl, hydroxy, sulfonic acid, (C₁-C₄)-dialkylamino residues, or R⁹ and R⁸ together form with the benzene moiety a condensed carbocyclic ring system, comprising 1 to 3 six membered rings, which may bear at least one group selected from hydroxy or sulfonic acid residues.

9. Liquid aqueous composition according to any of the preceding claims comprising colorant dyes in an amount of from 0.0001% to 1% by wt. of the liquid composition, preferably in an amount of from 0.001 to 0.4% by wt. of the composition.

5 10. Liquid aqueous composition according to any of the preceding claims comprising additionally at least one cationic surfactant.

10 11. A method of reducing destruction of colorant dye in a liquid composition in a bottle that is permeable for UV light which method comprises adding at least one organic phosphonic acid compound, having at least two phosphonic acid residues to said composition.

12. A method according to claim 11 **characterized in that** said composition has a pH-value of < 7 (at 20°C).

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REFERENCES CITED IN THE DESCRIPTION

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