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(54) **IMPROVED SHINE IN SOFT WATER**

(57) Hard surface cleaning composition comprising a water-soluble phosphono-chelant provide improved shine, even when cleaning using soft water.

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Description

FIELD OF THE INVENTION

5 **[0001]** Chelants providing improved shine even when cleaning hard surfaces with soft water.

BACKGROUND OF THE INVENTION

10 **[0002]** Hard surface cleaning compositions are used for cleaning and treating hard surfaces. Preferably, the hard surface cleaning composition is formulated to be an "all purpose" hard surface cleaning composition. That is, the hard surface cleaning composition is formulated to be suitable for cleaning as many different kinds of surfaces as possible.

15 **[0003]** High surface shine results in a better impression of surface cleanliness. As such, the users demand good surface shine after treatment of surfaces using hard surface cleaning compositions. It is well known that water hardness can impact surface shine due to the deposition of insoluble inorganic crystals. As such, chelants and sequestering agents, including phosphates and phosphonates, have been added to hard surface cleaning compositions to remove water hardness.

[0004] However, the level of shine after treating the surface is also less than desired when cleaned with hard surface cleaning compositions and soft water. It is believed that this is due to residues left behind from the formulation, and redeposited soil.

20 **[0005]** Therefore, a need remains for a method of cleaning which imparts improved shine after washing the hard surface using soft water.

[0006] US 6268324 B1 and US 6630434 B2 (Ecolab) relate to aqueous cleaning compositions providing increasing viscosity upon dilution. US 6268324 B1 discloses the cleaning of metal surfaces using compositions comprising 2-phosphonobutane-1,2,4,-tricarboxylic acid, amongst other phosphono-chelants, and soft water, but does not mention improvements in shine. US 4,784,774 (B.F Goodrich Company) relates to antiscalant admixtures of a homopolymer of maleic acid or a copolymer and a phosphonoalkane carboxylic acid for reducing scaling in an aqueous system. WO2009/078867 A1 relates to degreasing compositions of surfactant-based products containing anionic and nonionic surfactants, one or more sequestering agents, a glycol solvent for the preparation of liquid cleaning compositions. US2010/0331227 relates to hydrogen peroxide cleaning and sanitizing solutions consisting of distilled water, hydrogen peroxide, a surfactant, a hydrogen peroxide stabilizer, a chelating agent, and corrosion inhibitors. US6218349 relates to a composition suitable for removing proteinaceous material comprising water, an emulsifier, a chelating agent, one or more mineral acids, and a surfactant. WO 2013/055863 relates to chlorinated and non-chlorinated alkaline cleaning compositions for removal of proteinaceous and fatty soils at low temperature. WO 2012/028203 relates to a cleaning composition comprising a water-soluble aminopolycarboxylate and/or aminopolycarboxylic acid chelant, a carboxylate and/or organic carboxylic acid, a sequestering agent, a liquid conditioner polymer, and a solvent. EP-799612 relates to a detergent composition comprising a sulfate ester surfactant, at least one surfactant selected from amphoteric surfactants, amine oxide surfactants, alkanol amide surfactants and amide amino-acid surfactants, a cationic bactericide and a metal chelating agent. EP2245128 relates to compositions of surfactant-based products containing anionic and nonionic surfactants, one or more sequestering agents, a glycol solvent for the preparation of liquid cleaning compositions. US2014/0148371 and US2014/0148372 relate to alkaline or neutral viscoelastic cleaning compositions which use non polymer thickening agents. WO2001/000760 relates to organic compositions for removing complex organic soils from wood, metal and other hard surfaces, which comprise nonionic surfactants, silicone surfactants, hydrotropes and other optional functional materials such as sequestrants. WO2003/018733 relates to a low foaming surfactant blend for use in highly alkaline conditions including at least one C3 to C10 alkyl polyglucoside, at least one amine oxide, at least one polycarboxylated alcohol alkoxylate, and at least one alcohol alkoxylate. EP2447349 A1 relates to a thickened alkaline liquid hard surface cleaning composition comprising a surfactant system and chelant to provide cleaning and shine. WO 2004/013271 A1 relates to aqueous cleaning agents used to treat hard surfaces, containing at least one surfactant, one ethoxylated triglyceride and one hydrophilizing agent.

50 SUMMARY OF THE INVENTION

[0007] The present invention relates to the use of a phosphono-chelant in a wash liquor comprising a hard surface cleaning composition and soft water, for improving shine of hard surfaces. The present invention further relates to a method of cleaning and shining a hard surface, comprising the steps of diluting a hard surface cleaning composition with water having a water hardness of less than 1.5 mmol/l, the hard surface cleaning composition comprising a phosphono-chelant, then applying the diluted composition to a hard surface and optionally rinsing.

DETAILED DESCRIPTION OF THE INVENTION

[0008] It has surprisingly been found that phosphonochelants, when used in hard surface cleaning compositions, improve the shine of treated surfaces when cleaning with soft water.

[0009] As defined herein, "essentially free of" a component means that no amount of that component is deliberately incorporated into the composition. Preferably, "essentially free of" a component means that no amount of that component is present in the composition.

[0010] All percentages, ratios and proportions used herein are by weight percent of the premix, unless otherwise specified. All average values are calculated "by weight" of the composition, unless otherwise expressly indicated.

[0011] All ratios are calculated as a weight/weight level, unless otherwise specified.

[0012] All measurements are performed at 25°C unless otherwise specified.

[0013] Unless otherwise noted, all component or composition levels are in reference to the active portion of that component or composition, and are exclusive of impurities, for example, residual solvents or by-products, which may be present in commercially available sources of such components or compositions.

Liquid hard surface cleaning compositions:

[0014] By "liquid hard surface cleaning composition", it is meant herein a liquid composition for cleaning hard surfaces found in households, especially domestic households. Surfaces to be cleaned include kitchens and bathrooms, e.g., floors, walls, tiles, windows, cupboards, sinks, showers, shower plastified curtains, wash basins, WCs, fixtures and fittings and the like made of different materials like ceramic, vinyl, no-wax vinyl, linoleum, melamine, glass, steel, kitchen work surfaces, any plastics, plastified wood, metal or any painted or varnished or sealed surface and the like. Household hard surfaces also include household appliances including, but not limited to refrigerators, freezers, washing machines, automatic dryers, ovens, microwave ovens, dishwashers and so on. Such hard surfaces may be found both in private households as well as in commercial, institutional and industrial environments.

[0015] The liquid compositions herein are generally aqueous compositions. Therefore, they may comprise from 30% to 99.5% by weight of the total composition of water, preferably from 50% to 98% and more preferably from 80% to 97%.

[0016] The pH is preferably from 7.0 to 12, more preferably from 7.5 to 11.5, even more preferably from 9.5 to 11.3, most preferably 10 to 11. It is believed that the greasy soil and particulate greasy soil cleaning performance is further improved at these preferred alkaline pH ranges. Accordingly, the compositions herein may further comprise an acid or base to adjust pH as appropriate.

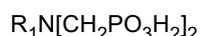
[0017] A suitable acid for use herein is an organic and/or an inorganic acid. A preferred organic acid for use herein has a pKa of less than 6. A suitable organic acid is selected from the group consisting of: citric acid, lactic acid, glycolic acid, succinic acid, glutaric acid and adipic acid and mixtures thereof. A suitable inorganic acid can be selected from the group consisting of: hydrochloric acid, sulphuric acid, phosphoric acid and mixtures thereof. A typical level of such acids, when present, is from 0.01% to 5.0% by weight of the total composition, preferably from 0.04% to 3.0% and more preferably from 0.05% to 1.5 %.

[0018] A suitable base to be used herein is an organic and/or inorganic base. Suitable bases for use herein are the caustic alkalis, such as sodium hydroxide, potassium hydroxide and/or lithium hydroxide, and/or the alkali metal oxides such, as sodium and/or potassium oxide or mixtures thereof. A preferred base is a caustic alkali, more preferably sodium hydroxide and/or potassium hydroxide. Other suitable bases include ammonia, ammonium carbonate, K_2CO_3 , Na_2CO_3 and alkanolamines (such as monoethanolamine, triethanolamine, aminomethylpropanol, and mixtures thereof). Typical levels of such bases, when present, are from 0.01% to 5.0% by weight of the total composition, preferably from 0.05% to 3.0% and more preferably from 0.1% to 2.0 %.

[0019] Hard surface cleaning compositions typically do not contain intentionally added magnesium or calcium ions. That is, added other than as trace by-products in any of the constituent raw materials.

Water-soluble organic phosphonic acid or salt thereof:

[0020] The compositions of use in the present invention comprise a phosphono-chelant. Suitable water-soluble organic phosphonic acids or salts thereof can have the formula:



wherein R_1 is:

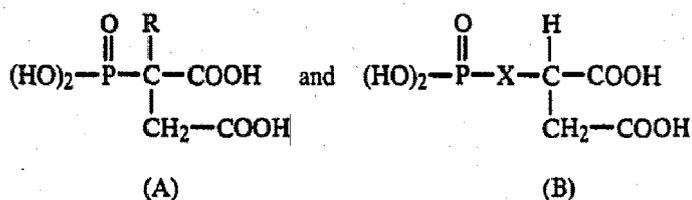
- [(lower)alkyl]N[CH₂PO₃H₂]₂ or salt thereof, or
- [(lower)alkyl]N[CH₂PO₃H₂][(lower)alkyl]N[CH₂PO₃H₂]₂ or salt thereof,

- $[\text{CH}_2\text{PO}_3\text{H}_2]$ moiety or salt thereof.

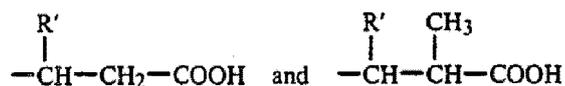
[0021] Preferably, R_1 is $-[(\text{lower})\text{alkyl}]\text{N}[\text{CH}_2\text{PO}_3\text{H}_2][(\text{lower})\text{alkyl}]\text{N}[\text{CH}_2\text{PO}_3\text{H}_2]_2$ or salt thereof. Suitable lower alkyl groups include those with the main hydrocarbon chain containing at least 2, preferably 2 to 8, more preferably 2 to 4 carbon atoms, optionally with substituents on the chain selected from alkyl, alkenyl, alkynyl, aryl, aralkyl, and carboxylic and halogenated versions thereof. Most preferably, the (lower)alkyl groups are $-\text{C}_2\text{H}_4-$ ethyl groups.

[0022] Suitable organic phosphonic acid sodium salts include 1-hydroxyethylidene-1,1-diphosphonic acid ($\text{CH}_3\text{C}(\text{PO}_3\text{H}_2)_2\text{OH}$, HEDP) and its sodium salt, available from Monsanto Industrial Chemicals Co., Missouri, USA. as Dequest® 2016, a 58-62% aqueous solution; amino [tri(methylenephosphonic acid)] ($\text{N}[\text{CH}_2\text{PO}_3\text{H}_2]_3$) or salt thereof, available from Monsanto as Dequest® 2000, a 50% aqueous solution; ethylenediamine [tetra(methylene-phosphonic acid)] available from Monsanto as Dequest® 2041, a 90% solid acid product, and , diethylenetriamine penta(methylene phosphonic acid) (DTPMP).

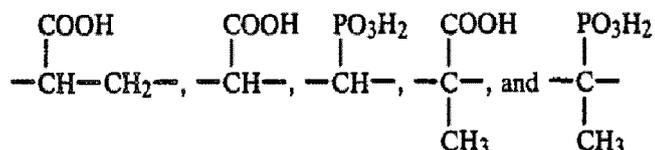
[0023] The phosphonocarboxylic acids, or salts thereof, can include those of formula (A) and (B):



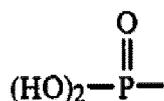
wherein R is hydrogen, alkyl, alkenyl, or alkynyl radical having 1 to 4 carbon atoms, an aryl, cycloalkyl, or aralkyl radical, or the radical selected from the following:



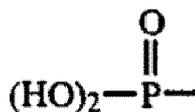
wherein R' is hydrogen, alkyl radical of 1 to 4 carbon atoms, or a carboxyl radical; and X is selected from the following:



wherein the $-\text{PO}_3\text{H}_2$ group is the phosphono group:



[0024] Suitable Water-soluble organic phosphonic acid or salt thereof include low molecular weight phosphonopoly-carboxylic acids such as one having 2-4 carboxylic acid moieties and about 1-3 phosphonic acid groups. Illustrative of specific phosphonocarboxylic acids include 1-phosphono-1-methylsuccinic acid, phosphonosuccinic acid, 1-phosphonopropane-2,3-dicarboxylic acid, 2-phosphonobutane-1,2,4-tricarboxylic acid, α -allyl-phosphonosuccinic acid, α -p-chloro-phenylphosphonosuccinic acid, α -propargyl-phosphonosuccinic acid, α -benzyl-phosphonosuccinic acid, α -cyclohexyl-phosphonosuccinic acid, 2-phosphono-3-(α -methyl-carboxymethyl-hexane-1,2,4-tricarboxylic acid, 2,2-diphosphono-butane-4-dicarboxylic acid, and the like. The preferred phosphonocarboxylic acids are 1-phosphono-1-methylsuccinic acid, phosphonosuccinic acid and 2-phosphonobutane-1,2,4-tricarboxylic acid, in particular, 2-phosphonobutane-1,2,4-tricarboxylic acid (available from Mobay Chemical Corporation, Inorganic Chemicals Division, Pittsburgh, Pa. as Bayhibit AM, a 45-50% aqueous solution). The phosphonocarboxylic acids, which are also typically referred to as phosphonoalkane carboxylic acids and phosphono lower alkyl carboxylic acids, contain at least one and preferably one or two phosphono groups:



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[0025] Preferably at least two and more preferably two or three carboxylic acid groups, with the main hydrocarbon chain containing at least 2, preferably 2 to 8, more preferably 2 to 4 carbon atoms, optionally with substituents on the chain selected from alkyl, alkenyl, alkynyl, aryl, aralkyl, and carboxylic and halogenated versions thereof.

10 **[0026]** The above-mentioned phosphonic acids can also be used in the form of water-soluble acid salts, particularly the alkali metal salts, such as sodium or potassium; the ammonium salts or the alkylol amine salts where the alkylol has 2 to 3 carbon atoms, such as mono-, di-, or triethanolamine salts. If desired, mixtures of the individual phosphonic acids or their acid salts can also be used. Phosphonic acids are discussed in U.S. Pat. No. 4,051,058.

15 **[0027]** Preferred water-soluble organic phosphonic acid or salts can be selected from the group consisting of: 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP), diethylenetriamine penta(methylene phosphonic acid) (DTPMP), 2-phosphonobutane-1,2,4-tricarboxylic acid, or salts thereof, and mixtures thereof, preferably 2-phosphonobutane-1,2,4-tricarboxylic acid, or salts thereof.

Surfactant

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[0028] The total amount of surfactant is from 0.1 to 25, preferably 2 to 20, more preferably from 3 to 15 and most preferably from 5 to 12% by weight of the composition. Preferred surfactants include non-ionic surfactant, anionic surfactant, and combinations thereof, though additional surfactants can be present.

25 Non-ionic surfactant

[0029] The liquid hard surface cleaning composition preferably comprises a non-ionic surfactant. The non-ionic surfactant can be selected from the group consisting of: alkoxyated non-ionic surfactants, alkyl polyglycosides, amine oxides, and mixture thereof. Typically, the liquid hard surface cleaning composition can comprise from 1.0 wt% to 10.0 wt% by weight of the total composition of said non-ionic surfactant, preferably from 3.0 wt% to 9.5 wt%, more preferably from 4.0 wt% to 9.0 wt% and most preferably from 5.0 wt% to 8.0 wt%.

[0030] The hard surface cleaning composition can comprise from 1 wt% to 10 wt%, preferably from 1.5wt% to 8 wt%, more preferably from 2 wt% to 7 wt% and most preferably from 2 wt% to 6 wt% of the composition of alkoxyated alcohol, preferably ethoxyated alcohol.

35 **[0031]** Suitable alkoxyated non-ionic surfactants include primary C₆-C₁₆ alcohol polyglycol ether i.e. ethoxyated alcohols having 6 to 16 carbon atoms in the alkyl moiety and 4 to 30 ethylene oxide (EO) units. When referred to for example C₉₋₁₄ it is meant average carbons and alternative reference to for example EO8 is meant average ethylene oxide units.

[0032] Suitable ethoxyated non-ionic surfactants for use herein are Dobanol® 91-2.5 (HLB = 8.1; R is a mixture of C₉ and C₁₁ alkyl chains, n is 2.5), Dobanol® 91-10 (HLB = 14.2; R is a mixture of C₉ to C₁₁ alkyl chains, n is 10), Dobanol® 91-12 (HLB = 14.5; R is a mixture of C₉ to C₁₁ alkyl chains, n is 12), Greenbentine DE80 (HLB = 13.8, 98 wt% C₁₀ linear alkyl chain, n is 8), Marlipal 10-8 (HLB = 13.8, R is a C₁₀ linear alkyl chain, n is 8), Lialethl® 11-5 (R is a C₁₁ alkyl chain, n is 5), Isalchem® 11-5 (R is a mixture of linear and branched C₁₁ alkyl chain, n is 5), Lialethl® 11-21 (R is a mixture of linear and branched C₁₁ alkyl chain, n is 21), Isalchem® 11-21 (R is a C₁₁ branched alkyl chain, n is 21), Empilan® KBE21 (R is a mixture of C₁₂ and C₁₄ alkyl chains, n is 21) or mixtures thereof. Preferred herein are Dobanol® 91-5, Neodol® 11-5, Lialethl® 11-21 Lialethl® 11-5 Isalchem® 11-5 Isalchem® 11-21 Dobanol® 91-8, or Dobanol® 91-10, or Dobanol® 91-12, or mixtures thereof. These Dobanol®/Neodol® surfactants are commercially available from SHELL. The Greenbentine® surfactant is commercially available from KOLB. These Isalchem®/Marlipal® surfactants are commercially available from Sasol. The Empilan® surfactants are commercially available from Huntsman.

50 **[0033]** Preferably, said alkoxyated non-ionic surfactant is a C₉₋₁₁ EO5 alkylethoxylate, C₁₂₋₁₄ EO5 alkylethoxylate, a C₁₁ EO5 alkylethoxylate, C₁₂₋₁₄ EO21 alkylethoxylate, or a C₉₋₁₁ EO8 alkylethoxylate or a mixture thereof. Most preferably, said alkoxyated non-ionic surfactant is a C₁₁ EO5 alkylethoxylate or a C₉₋₁₁ EO8 alkylethoxylate or a mixture thereof.

[0034] Suitable amine oxide surfactants include amine oxides having the following formula: R₁R₂R₃NO wherein R₁ is an hydrocarbon chain comprising from 1 to 30 carbon atoms, preferably from 6 to 20, more preferably from 8 to 16 and wherein R₂ and R₃ are independently saturated or unsaturated, substituted or unsubstituted, linear or branched hydrocarbon chains comprising from 1 to 4 carbon atoms, preferably from 1 to 3 carbon atoms, and more preferably are methyl groups. R₁ may be a saturated or unsaturated, substituted or unsubstituted linear or branched hydrocarbon chain. Preferably, the liquid hard surface cleaning composition comprises from 0.05 wt % to 6 wt%, preferably from 0.1 wt%

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to 5 wt%, more preferably from 0.1 wt% to 4.5 wt% and most preferably from 0.1 wt% to 4 wt% of the composition of amine oxide surfactant.

[0035] A highly preferred amine oxide is C₁₂-C₁₄ dimethyl amine oxide, commercially available from Albright & Wilson, C₁₂-C₁₄ amine oxides commercially available under the trade name Genaminox® LA from Clariant or AROMOX® DMC from AKZO Nobel.

[0036] The non-ionic surfactant is preferably a low molecular weight non-ionic surfactant, having a molecular weight of less than 950 g/mol, more preferably less than 500 g/mol.

Anionic surfactant:

[0037] The liquid hard surface cleaning composition can comprise an anionic surfactant. The anionic surfactant can be selected from the group consisting of: alkyl sulphate, alkyl alkoxyated sulphate, sulphonic acid or sulphonate surfactant, and mixtures thereof. The liquid hard surface cleaning composition can comprise from 0.05 wt% to 5 wt%, preferably from 0.1 wt% to 4 wt%, and most preferably from 1.5 wt% to 3.5 wt% of anionic surfactant.

[0038] Suitable alkyl sulphates for use herein include water-soluble salts or acids of the formula ROSO₃M wherein R is a C₆-C₁₈ linear or branched, saturated or unsaturated alkyl group, preferably a C₈-C₁₆ alkyl group and more preferably a C₁₀-C₁₆ alkyl group, and M is H or a cation, e.g., an alkali metal cation (e.g., sodium, potassium, lithium), or ammonium or substituted ammonium (e.g., methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations, such as tetramethyl-ammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like).

[0039] Particularly suitable linear alkyl sulphates include C₁₂₋₁₄ alkyl sulphate like EMPICOL® 0298/, EMPICOL® 0298/F or EMPICOL® XLB commercially available from Huntsman.

[0040] Suitable sulphonated anionic surfactants can be selected from the group consisting of: alkyl sulphonates; alkyl aryl sulphonates; naphthalene sulphonates; alkyl alkoxyated sulphonates; and C₆-C₁₆ alkyl alkoxyated linear or branched diphenyl oxide disulphonates; and mixtures thereof.

[0041] Suitable alkyl sulphonates for use herein include water-soluble salts or acids of the formula RSO₃M wherein R is a C₆-C₁₈ linear or branched, saturated or unsaturated alkyl group, preferably a C₈-C₁₆ alkyl group and more preferably a C₁₀-C₁₆ alkyl group, and M is H or a cation, e.g., an alkali metal cation (e.g., sodium, potassium, lithium), or ammonium or substituted ammonium (e.g., methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations, such as tetramethyl-ammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like).

[0042] Suitable alkyl aryl sulphonates for use herein include water-soluble salts or acids of the formula RSO₃M wherein R is an aryl, preferably a benzyl, substituted by a C₆-C₁₈ linear or branched saturated or unsaturated alkyl group, preferably a C₈-C₁₆ alkyl group and more preferably a C₁₀-C₁₆ alkyl group, and M is H or a cation, e.g., an alkali metal cation (e.g., sodium, potassium, lithium, and the like) or ammonium or substituted ammonium (e.g., methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations, such as tetramethyl-ammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like).

[0043] By "linear alkyl sulphonate" it is meant herein a non-substituted alkyl sulphonate wherein the alkyl chain comprises from 6 to 18 carbon atoms, preferably from 8 to 16 carbon atoms, and more preferably from 10 to 16 carbon atoms, and wherein this alkyl chain is sulphonated at one terminus.

[0044] Suitable alkoxyated sulphonate surfactants for use herein are according to the formula R(A)_mSO₃M, wherein R is an unsubstituted C₆-C₁₈ alkyl, hydroxyalkyl or alkyl aryl group, having a linear or branched C₆-C₁₈ alkyl component, preferably a C₈-C₁₆ alkyl or hydroxyalkyl, more preferably C₁₂-C₁₆ alkyl or hydroxyalkyl, and A is an ethoxy or propoxy or butoxy unit, and m is greater than zero, typically between 0.5 and 6, more preferably between 0.5 and 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, etc.), ammonium or substituted-ammonium cation. Optional ingredients:

Thickener: The liquid hard surface cleaning composition can comprise a thickener. An increased viscosity, especially low shear viscosity, provides longer contact time and therefore improved penetration of greasy soil and/or particulated greasy soil to improve cleaning effectiveness, especially when applied neat to the surface to be treated. Moreover, a high low shear viscosity improves the phase stability of the liquid cleaning composition, and especially improves the stability of the copolymer in compositions in the liquid hard surface cleaning composition. Hence, preferably, the liquid hard surface cleaning composition, comprising a thickener, has a viscosity of from 50 Pa.s to 650 Pa.s, more preferably 100 Pa.s to 550 Pa.s, most preferably 150 Pa.s to 450 Pa.s, at 20°C when measured with a AD1000 Advanced Rheometer from Atlas® shear rate 10 s⁻¹ with a coned spindle of 40mm with a cone angle 2° and a truncation of ±60µm. Suitable thickeners include polyacrylate based polymers, preferably hydrophobically modified polyacrylate polymers; hydroxyl ethyl cellulose, preferably hydrophobically modified hydroxyl ethyl cellulose, xanthan

gum, hydrogenated castor oil (HCO) and mixtures thereof.

[0045] Preferred thickeners are polyacrylate based polymers, preferably hydrophobically modified polyacrylate polymers. Preferably a water soluble copolymer based on main monomers acrylic acid, acrylic acid esters, vinyl acetate, methacrylic acid, acrylonitrile and mixtures thereof, more preferably copolymer is based on methacrylic acid and acrylic acid esters having appearance of milky, low viscous dispersion. Most preferred hydrologically modified polyacrylate polymer is Rheovis® AT 120, which is commercially available from BASF.

[0046] When used, the liquid hard surface cleaning composition comprises from 0.1% to 10.0% by weight of the total composition of said thickener, preferably from 0.2% to 5.0%, more preferably from 0.2% to 2.5% and most preferably from 0.2% to 2.0%.

[0047] *Additional Surfactant:* The hard surface cleaning composition may comprise up to 10% by weight of an additional surfactant, preferably selected from: an amphoteric, zwitterionic, and mixtures thereof. More preferably, the hard surface cleaning composition can comprise from 0.5% to 5%, or from 0.5% to 3%, or from 0.5% to 2% by weight of the additional surfactant. *Additional chelating agent:* The composition can comprise up to 2.0 wt%, preferably from 0.05% to 1.0%, preferably from 0.1 to 0.5% by weight of one or more additional chelant. While such amounts of additional chelants provide improved chelation, it has been found that higher levels of the additional chelants reduce surface shine. Suitable additional chelant can be selected from the group consisting of: citric acid, and catechol sulfonates such as Tiron™ and mixtures thereof.

[0048] *Cleaning polymer:* The liquid hard surface cleaning composition may comprise a cleaning polymer. For instance, Suitable polymers can improve the grease removal performance of the liquid composition due to the specific sudsing/foaming characteristics they provide to the composition. Suitable polymers for use herein are disclosed in EP patent application EP2272942 (09164872.5) and granted European patent EP2025743 (07113156.9).

[0049] The polymer can be selected from the group consisting of: a vinylpyrrolidone homopolymer (PVP); a polyethyleneglycol dimethylether (DM-PEG); a vinylpyrrolidone/dialkylaminoalkyl acrylate or methacrylate copolymers; a polystyrenesulphonate polymer (PSS); a poly vinyl pyridine-N-oxide (PVNO); a polyvinylpyrrolidone/ vinylimidazole copolymer (PVP-VI); a polyvinylpyrrolidone/ polyacrylic acid copolymer (PVP-AA); a polyvinylpyrrolidone/ vinylacetate copolymer (PVP-VA); a polyacrylic polymer or polyacrylicmaleic copolymer; and a polyacrylic or polyacrylic maleic phosphono end group copolymer; and mixtures thereof. Typically, the liquid hard surface cleaning composition may comprise from 0.005% to 5.0% by weight of the total composition of said polymer, preferably from 0.10% to 4.0%, more preferably from 0.1% to 3.0% and most preferably from 0.20% to 1.0%.

[0050] *Fatty acid:* The liquid hard surface cleaning composition may comprise a fatty acid as a highly preferred optional ingredient, particularly as suds suppressors. Fatty acids are desired herein as they reduce the sudsing of the liquid composition when the composition is rinsed off the surface to which it has been applied.

[0051] The liquid hard surface cleaning composition may comprise a branched fatty alcohol, particularly as suds suppressors. Suitable branched fatty alcohols include the 2-alkyl alkanols having an alkyl chain comprising from 6 to 16, preferably from 7 to 13, more preferably from 8 to 12, most preferably from 8 to 10 carbon atoms and a terminal hydroxy group, said alkyl chain being substituted in the α position (i.e., position number 2) by an alkyl chain comprising from 1 to 10, preferably from 2 to 8 and more preferably 4 to 6 carbon atoms.

[0052] Typically, the liquid hard surface cleaning composition may comprise up to 6.0% by weight of the total composition of said fatty acid, preferably from 0.1% to 3.0%, more preferably from 0.1% to 2.0% and most preferably from 0.15% to 1.5% by weight of the total composition of said fatty acid.

[0053] *Solvent:* The liquid hard surface cleaning compositions preferably comprises a solvent. Suitable solvents may be selected from the group consisting of: ethers and diethers having from 4 to 14 carbon atoms; glycols or alkoxyated glycols; alkoxyated aromatic alcohols; aromatic alcohols; alkoxyated aliphatic alcohols; aliphatic alcohols; C₈-C₁₄ alkyl and cycloalkyl hydrocarbons and haloalkyl hydrocarbons; C₆-C₁₆ glycol ethers; terpenes; and mixtures thereof.

[0054] *Other optional ingredients:* The liquid hard surface cleaning compositions may comprise a variety of other optional ingredients depending on the technical benefit aimed for and the surface treated. Suitable optional ingredients for use herein include perfume, builders, other polymers, buffers, bactericides, hydrotropes, colorants, stabilisers, radical scavengers, abrasives, soil suspenders, brighteners, anti-dusting agents, dispersants, dye transfer inhibitors, pigments, silicones and/or dyes.

Method of cleaning and shining a hard surface:

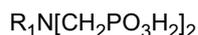
[0055] Liquid hard surface cleaning compositions comprising the phosphonochelant and preferably at least one detergent surfactant, especially the compositions of the present invention, are suitable for cleaning household surfaces. In particular, such compositions are particularly useful for cleaning and improving shine on hard surfaces, including hard surfaces selected from the group consisting of: ceramic, stone, laminate flooring, linoleum, and the like. Suitable detergent surfactants can be selected from the group consisting of: anionic surfactant, non-ionic surfactant, and mixtures thereof.

[0056] For general cleaning and improving shine on a hard surface, the preferred method of cleaning comprises the steps of:

- 5 (a) diluting a hard surface cleaning composition with water having a water hardness of less than 1.5 mmol/l, the hard surface cleaning composition comprising the phosphonochelant.
 (b) applying the diluted composition to a hard surface, and
 (c) optionally rinsing.

[0057] Suitable phosphonochelants include those selected from the group consisting of:

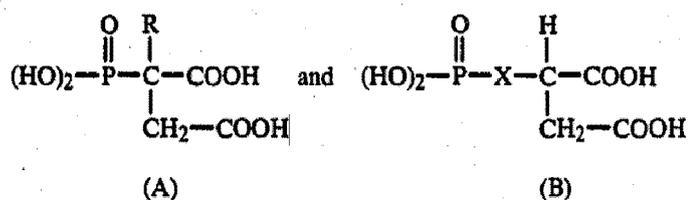
10 water-soluble organic phosphonic acids or salts thereof can have the formula:



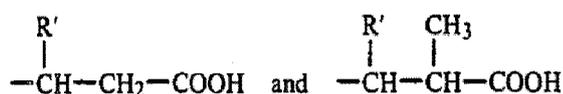
15 wherein R₁ is:

- [(lower)alkyl]N[CH₂PO₃H₂]₂ or salt thereof, or
 - [(lower)alkyl]N[CH₂PO₃H₂][(lower)alkyl]N[CH₂PO₃H₂]₂ or salt thereof,
 - [CH₂PO₃H₂] moiety or salt thereof,

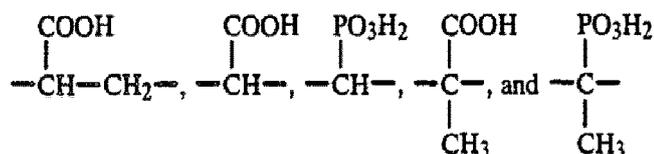
20 phosphonocarboxylic acids, or salts thereof, including those of formula (A) and (B):



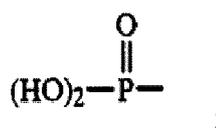
wherein R is hydrogen, alkyl, alkenyl, or alkynyl radical having 1 to 4 carbon atoms, an aryl, cycloalkyl, or aralkyl radical, or the radical selected from the following:



40 wherein R' is hydrogen, alkyl radical of 1 to 4 carbon atoms, or a carboxyl radical; and X is selected from the following:



wherein the -PO₃H₂ group is the phosphono group:



and mixtures thereof.

[0058] The liquid hard surface composition can be formulated as a spray. As such, the liquid hard surface cleaning

composition can be applied to the hard surface via spraying.

[0059] In particular embodiments, the liquid hard surface cleaning composition may be diluted to a level of from 0.3% to 1.6%, or to 1.5% by volume. The liquid hard surface cleaning composition may be diluted to a level of from 0.4% to 0.6% by volume, especially where the liquid hard surface cleaning composition has a total surfactant level of greater than or equal to 5% by weight. Where the liquid hard surface cleaning composition has a total surfactant level of less than 5% by weight, the liquid hard surface cleaning composition may be diluted to a level of from 0.7% to 1.6% or to 1.4% by volume.

[0060] The liquid hard surface cleaning composition is diluted with water having a hardness of less than 1.5, preferably less than 1.0 mmol/l, more preferably less than 0.5 mmol/l.

[0061] The dilution level is expressed as a percent defined as the fraction of the liquid hard surface cleaning composition, by volume, with respect to the total amount of the diluted composition. For example, a dilution level of 5% by volume is equivalent to 50 ml of the liquid hard surface cleaning composition being diluted to form 1000 ml of diluted composition.

[0062] The diluted composition can be applied by any suitable means, including using a mop, sponge, or other suitable implement.

[0063] The hard surface may be rinsed, preferably with clean water, in an optional further step. More preferably, the hard surface is rinsed with water having a hardness of less than 1.5, preferably less than 1.0 mmol/l, more preferably less than 0.5 mmol/l.

[0064] By "neat", it is to be understood that the liquid composition is applied directly onto the surface to be treated without undergoing any significant dilution, i.e., the liquid composition herein is applied onto the hard surface as described herein, either directly or via an implement such as a sponge, without first diluting the composition. As such, the composition is diluted by less than 10 wt%, preferably by less than 5 wt%, more preferably by less than 3 wt% of the original composition volume. Such dilutions can arise from the use of damp implements to apply the composition to the hard surface, such as sponges which have been "squeezed" dry.

[0065] In another preferred embodiment of the present invention said method of cleaning a hard surface includes the steps of applying, preferably spraying, said liquid composition onto said hard surface, leaving said liquid composition to act onto said surface for a period of time to allow said composition to act, with or without applying mechanical action, and optionally removing said liquid composition, preferably removing said liquid composition by rinsing said hard surface with water and/or wiping said hard surface with an appropriate instrument, e.g., a sponge, a paper or cloth towel and the like.

Methods:

A) pH measurement:

[0066] The pH is measured on the neat composition, at 25°C, using a Sartorius PT-10P pH meter with gel-filled probe (such as the Toledo probe, part number 52 000 100), calibrated according to the instructions manual.

B) Shine test for floor cleaning:

[0067] The composition was diluted to a level of 0.48 wt% using water having the desired hardness level.

[0068] Black glossy tiles (20cm x 25 cm reference H07300 Sphinx ceramic tiles) are soaked in a nilpolymer APC solution overnight, rinsed and dried. The tiles are sprayed with a soil blend comprising vegetable oil, polymerized vegetable oil, sugar and house dust (18:2:29:51 blend in isopropanol alcohol) until 0.015 g of the soil has been applied and the tile dried. The tiles are then cleaned using a non-woven cloth soaked in the diluted cleaning solution, first horizontally, then vertically, and then again horizontally. The cloth is then rinsed in the diluted cleaning solution, and the tiles cleaned in the same manner, using the other side of the nonwoven cloth. The tiles are then graded using the grading scale described below. A lower value means better shine:

Grading scale:

- 0= as new /no streaks and/or film
- 1= very slight streaks and/or film
- 2= slight streaks and/or film
- 3= slight to moderate streaks and/or film
- 4= moderate streaks and/or film
- 5= moderate/heavy streaks and/or film
- 6= heavy streaks and/or film

EXAMPLES

[0069] Formulation was prepared by simple mixing, leaving a 0.5wt% "hole" in the formulation for the chelant.

5		Formulation A wt%
	C9/11 EO8 ¹	6.2
	HLAS	1.8
10	C12-14 Amine Oxide ²	1.5
	Hydrophobically modified-polyacrylate ³	0.70
	Na ₂ CO ₃	0.75
	Citric Acid	0.30
15	Sodium Hydroxide	0.65
	TPK fatty acid	0.4
	Minors and Water	to 99.5%
20	pH	10.3
	¹ nonionic surfactant commercially available from Shell. ² amine oxide nonionic surfactant commercially available from Huntsman ³ Rheovis AT 120 thickener commercially available from BASF	

25 [0070] To the formulation was added the following chelants, at a level of 0.5 wt% chelant in the finished formula, in order to make examples 1 to 3 and examples A and B. Examples 1 to 3 comprised chelants which were of use in the present invention. Comparative examples A and B comprised alternative chelants. Comparative example C, comprised no chelant. The compositions were diluted using water of different hardness levels, and used to clean soiled tiles, and the resultant shine assessed using the method described above using the nil-chelant (comparative example F) as the reference:

	Ex 1 wt%	Ex 2 wt%	Ex 3 wt%	Ex A* wt%	Ex B* wt%	Ex C* wt%	
35	formulation A	99.5	99.5	99.5	99.5	99.5	
	diethylenetriamine penta (methylene phosphonic acid) ⁴	0.5	-	-	-	-	
40	1-hydroxyethane 1,1-diphosphonic acid ⁵	-	0.5	-	-	-	
	2-Phosphonobutane -1,2,4-tricarboxylic Acid ⁶	-	-	0.5	-	-	
	Methylglycinediacetic acid ⁷	-	-	-	0.5	-	
	Glutamic acid diacetic acid ⁸	-	-	-	-	0.5	
45	Water	-	-	-	-	0.5	
	Shine grade after washing using water at the following hardness levels:						
50	2.68 mmol/l	1.9	2.4	2.3	4.0	4.1	4.8
	1.07 mmol/l	1.5	2.3	2.3	5.1	4.8	4.8
	0.0000001 mmol/l	1.0	1.5	1.8	3.2	4.0	3.8
55	⁴ DTPMP, supplied by Giovanni Bozzetto SPA ⁵ HEDP, supplied by Alfa Aesar ⁶ PBTCA, supplied by BayHibit™ AM, available from LanXESS ⁷ MGDA, supplied by BASF ⁸ GLDA, supplied by Akzo Nobel						

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[0071] The compositions of comparative examples A and B, comprising alternative chelants, exhibit improved shine in comparison to the composition of example C which comprised no chelant, when used to wash the tiles using the composition in combination with hard water having a hardness of greater than 1.5 mmol/l. However, when the compositions of comparative examples A and B were used to wash tiles using the composition in combination with water having a lower hardness, the resultant shine was only moderately better or lower than when the nil-chelant composition of example C was used. In contrast, as can be seen from examples 1 to 3, when the phosphono-chelant is used, the improvement in shine is maintained even when cleaning using the composition in combination with water having a low water hardness. Hence, while shine is generally slightly improved through the use of water having lower water-hardness, it has surprisingly been discovered that the improvement in shine is greater when the phosphono-chelant is used instead of a comparative chelant.

[0072] The following are examples of liquid hard surface cleaning compositions suitable for use in the present invention:

	Ex 4 wt%	Ex 5 wt%	Ex 6 wt%	Ex 7 wt%	Ex 8 wt%	Ex 9 wt%	Ex 10 wt%
C9/11 EO8 ¹	6.0	2.5	7.0	-	-	6.0	6.0
C9/11EO5 ¹¹	-	-	-	3.5	-	-	-
C11EO5	-	-	-	-	7.0	-	-
C12/14EO21	-	-	-	3.5	-	-	-
NaLAS ¹²	2.00	0.75	1.8		-	-	2.25
NAPS ¹³	-	-	-	3.1	3.0	3.0	-
C12-14 Amine Oxide ¹⁴	1.50	0.25	1.50	3.9	2.0	-	1.25
C12-14 Betaine ¹⁵	-	-	-	-	1.0	3.0	-
Hydrophobically modified-polyacrylate ³	0.76	-	0.75	-	-	-	0.65
HM-HEC ¹⁶	-	-	-	0.6	0.8	-	-
Xanthan gum ¹⁷	-	-	-	-	-	0.42	-
Na ₂ CO ₃	0.77	0.9	0.75	0.1	0.3	0.2	0.4
Citric Acid	0.046	0.3	0.3	0.75	0.75	0.3	0.3
Caustic	0.46	0.2	0.72	0.5	0.5	0.3	0.65
TPK Fatty Acid	0.40	0.1	1.0	0.20	0.50	0.50	0.40
2-Phosphonobutane -1,2,4-tricarboxylic Acid ⁶	0.5	0.5	0.5	0.5	0.5	0.5	0.5
2-butyl octanol ¹⁸	-	-	0.1	0.2	0.3	0.5	-
IPA ¹⁹	-	-	-	-	-	2.0	-
n-BPP ²⁰	-	-	-	-	2.0	-	-
n-Bp ²¹	-	-	-	4.0	2.0	-	2.0
Minors and Water	up to 100%						

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(continued)

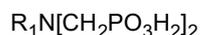
	Ex 4 wt%	Ex 5 wt%	Ex 6 wt%	Ex 7 wt%	Ex 8 wt%	Ex 9 wt%	Ex 10 wt%
pH	10.8	10.8	10.3	9.5	9	10.5	10.3
<p>11 nonionic surfactant commercially available from ICI or Shell. 12 sodium linear alkylbenzene sulphonate commercially available from Huntsman 13 sodium paraffin sulphonate commercially available from ICS 14 amine oxide nonionic surfactant commercially available from Huntsman 15 amphoteric surfactant commercially available from MC Intyre group 16 Hydrophobically modified hydroxyethylcellulose (cetylhydroxyethylcellulose) 17 commercially available from CP Kelco 18 commercially available from Sasol as Isofol 12® 19 isopropanol, commercially available from JT Baker 20 butoxypropoxypropanol, commercially available from Dow Chemicals 21 normal butoxy propanol commercially available from Dow Chemicals</p>							

[0073] The dimensions and values disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, each such dimension is intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as "40 mm" is intended to mean "about 40 mm".

Claims

- The use of a phosphono-chelant in a wash liquor comprising a hard surface cleaning composition and water having a hardness of less than 1.5 mmol/l, for improving shine of hard surfaces.
- The use according to claim 1, wherein the phosphono-chelant is selected from the group consisting of:

i. water-soluble organic phosphonic acids or salts thereof having the formula:

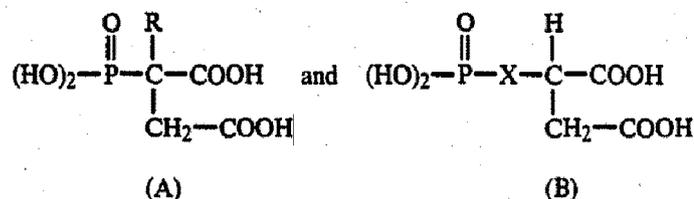


wherein R1 is a:

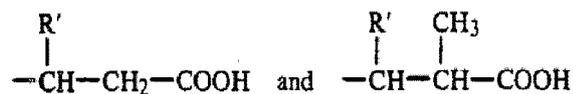
- [(lower)alkyl]N[CH₂PO₃H₂]₂ or salt thereof, or
- [(lower)alkyl]N[CH₂PO₃H₂][(lower)alkylene]N[CH₂PO₃H₂]₂ or salt thereof, or

a [CH₂PO₃H₂]₂ moiety or salt thereof;

ii. phosphonocarboxylic acids, or salts thereof, including those of formula (A) and (B):



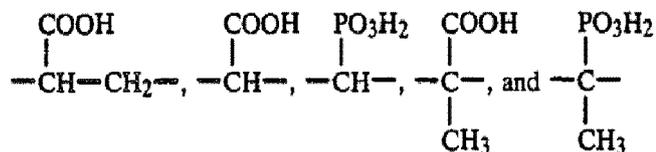
wherein R is hydrogen, alkyl, alkenyl, or alkynyl radical having 1 to 4 carbon atoms, an aryl, cycloalkyl, or aralkyl radical, or the radical selected from the following:



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wherein R' is hydrogen, alkyl radical of 1 to 4 carbon atoms, or a carboxyl radical; and X is selected from the following:

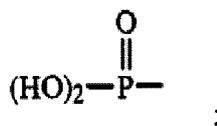
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wherein the -PO₃H₂ group is the phosphono group:

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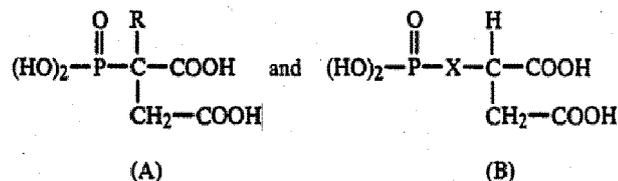


iii. and mixtures thereof.

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3. The use according to any preceding claims, wherein the chelant is selected from phosphonocarboxylic acids of formula (A) and (B), or their salts:

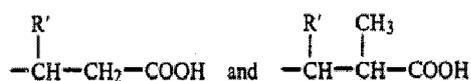
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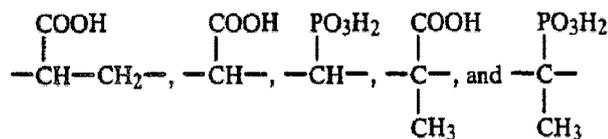
wherein R is hydrogen, alkyl, alkenyl, or alkynyl radical having 1 to 4 carbon atoms, an aryl, cycloalkyl, or aralkyl radical, or the radical selected from the following:

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wherein R' is hydrogen, alkyl radical of 1 to 4 carbon atoms, or a carboxyl radical; and X is selected from the following:

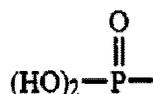
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wherein the -PO₃H₂ group is the phosphono group:

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4. The use according to any preceding claims, wherein the chelant is selected from the group consisting or: 1-hydrox-

yethylidene-1,1-diphosphonic acid (HEDP), diethylenetriamine penta(methylene phosphonic acid) (DTPMP), α -methylphosphonosuccinic acid, phosphonosuccinic acid, 1-phosphonopropane-2,3-dicarboxylic acid, 2-phosphonobutane-1,2,4-tricarboxylic acid, α -allyl-phosphonosuccinic acid, α -p-chloro-phenylphosphonosuccinic acid, α -propargyl-phosphonosuccinic acid, α -benzyl-phosphonosuccinic acid, α -cyclohexyl-phosphonosuccinic acid, 2-phosphono-3-(α -methyl-carboxymethyl-hexane-1,2,4-tricarboxylic acid, 2,2-diphosphono-butane-4-dicarboxylic acid, their salts, and mixtures thereof, preferably hydroxyethylidene-1,1-diphosphonic acid (HEDP), diethylenetriamine penta(methylene phosphonic acid) (DTPMP), 2-phosphonobutane-1,2,4-tricarboxylic acid, or salts thereof, and mixtures thereof, more preferably diethylenetriamine penta(methylene phosphonic acid) (DTPMP), 2-phosphonobutane-1,2,4-tricarboxylic acid, and salts thereof.

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11. The use according to any preceding claims, wherein the hard surface cleaning composition comprises from 1.0% to 20.0% by weight of a surfactant system.

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12. The use according to claim 5, wherein the surfactant system comprises surfactant selected from the group consisting of: alkoxylated nonionic surfactant, amine oxide surfactant, and mixtures thereof.

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13. The use according to claim 6, wherein the surfactant system comprises amine oxide surfactant at a level of up to 10%, preferably from 0.1 to 7.0%, more preferably from 0.15% to 3.0%, most preferably from 0.3% to 3.0% by weight of the total composition.

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14. The use according to any of claims 5 or 7, wherein the surfactant system comprises alkoxylated nonionic surfactant, preferably ethoxylated nonionic surfactant, at a level of from 1% to 10%, preferably from 1.5% to 8%, more preferably from 2% to 7% and most preferably from 2% to 6% by weight of the total composition.

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15. The use according to any preceding claims, wherein the soft water has a hardness of less than 1.0, preferably less than 0.5 mmol/l.

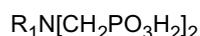
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16. The use according to any preceding claims, wherein the liquid hard surface cleaning composition is diluted to a level of from 0.3% to 1.5% by volume with the water.

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17. A method of cleaning and shining a hard surface, comprising the steps of:

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(a) diluting a hard surface cleaning composition with water having a water hardness of less than 1.5 mmol/l, the hard surface cleaning composition comprising a phosphono-chelant,
(b) applying the diluted composition to a hard surface,
(c) optionally without rinsing.

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18. The method according to claim 10, wherein the phosphono-chelant is selected the group consisting of:

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i. water-soluble organic phosphonic acids or salts thereof can have the formula:

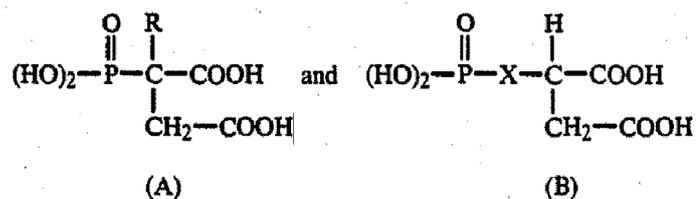


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wherein R1 is a:

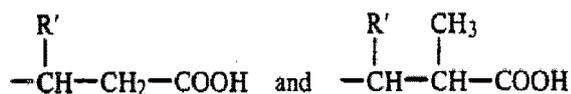
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- [(lower)alkyl]N[CH₂PO₃H₂]₂ or salt thereof, or
- [(lower)alkyl]N[CH₂PO₃H₂][(lower)alkylene]N[CH₂PO₃H₂]₂ or salt thereof, or

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a [CH₂PO₃H₂] moiety or salt thereof;

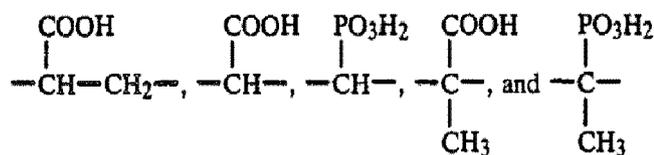
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ii. phosphonocarboxylic acids, or salts thereof, including those of formula (A) and (B):



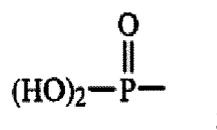
wherein R is hydrogen, alkyl, alkenyl, or alkynyl radical having 1 to 4 carbon atoms, an aryl, cycloalkyl, or aralkyl radical, or the radical selected from the following:



wherein R' is hydrogen, alkyl radical of 1 to 4 carbon atoms, or a carboxyl radical; and X is selected from the following:



wherein the $-\text{PO}_3\text{H}_2$ group is the phosphono group:



iii. and mixtures thereof.

13. The method according to any of claims 10 to 11, wherein the chelant is selected from the group consisting or: α -methylphosphonosuccinic acid, phosphonosuccinic acid, 1-phosphonopropane-2,3-dicarboxylic acid, 2-phosphonobutane-1,2,4-tricarboxylic acid, α -allyl-phosphonosuccinic acid, α -p-chloro-phenylphosphonosuccinic acid, α -propargyl-phosphonosuccinic acid, α -benzyl-phosphonosuccinic acid, α -cyclohexyl-phosphonosuccinic acid, 2-phosphono-3-(α -methyl-carboxymethyl-hexane-1,2,4-tricarboxylic acid, 2,2-diphosphono-butane-4-dicarboxylic acid, their salts, and mixtures thereof, preferably 2-phosphonobutane-1,2,4-tricarboxylic acid, or salt thereof.



EUROPEAN SEARCH REPORT

Application Number
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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X,D A	US 6 268 324 B1 (BESSE MICHAEL E [US] ET AL) 31 July 2001 (2001-07-31) * examples *	11-13 1-10	INV. C11D3/36 C11D11/00
X,D	EP 2 447 349 A1 (PROCTER & GAMBLE [US]) 2 May 2012 (2012-05-02) * paragraphs [0001], [0005], [0012], [0078] - [0080] * * examples * * claims *	1-13	
X,D	WO 2004/013271 A1 (HENKEL KGAA [DE]) 12 February 2004 (2004-02-12) * page 1, paragraph 1 * * page 2, paragraph 3-5 * * page 5, paragraph 6 * * examples; table 3 * * claims *	1-13	
A	DE 101 24 288 A1 (HENKEL KGAA [DE]) 28 November 2002 (2002-11-28) * paragraphs [0001], [0008], [0014] * * examples * * claims *	1-13	TECHNICAL FIELDS SEARCHED (IPC) C11D
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 22 September 2017	Examiner Bertran Nadal, Josep
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	

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

EP 17 16 2217

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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.

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6268324 B1	31-07-2001	AT 194380 T	15-07-2000
		AU 676066 B2	27-02-1997
		CA 2164127 A1	08-12-1994
		DE 69425142 D1	10-08-2000
		DE 69425142 T2	22-03-2001
		EP 0701601 A1	20-03-1996
		HK 1013095 A1	09-02-2001
		JP H08510772 A	12-11-1996
		NZ 268148 A	26-11-1996
		US 6268324 B1	31-07-2001
		US 2002082178 A1	27-06-2002
WO 9428108 A1	08-12-1994		
EP 2447349 A1	02-05-2012	CA 2816440 A1	03-05-2012
		EP 2447349 A1	02-05-2012
		ES 2551227 T3	17-11-2015
		RU 2013120423 A	10-12-2014
		US 2012102668 A1	03-05-2012
		WO 2012058250 A1	03-05-2012
WO 2004013271 A1	12-02-2004	AU 2003251451 A1	23-02-2004
		DE 10235089 A1	12-02-2004
		WO 2004013271 A1	12-02-2004
DE 10124288 A1	28-11-2002	NONE	

EPO FORM P0459

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

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- US 6268324 B1 [0006]
- US 6630434 B2 [0006]
- US 4784774 B [0006]
- WO 2009078867 A1 [0006]
- US 20100331227 A [0006]
- US 6218349 B [0006]
- WO 2013055863 A [0006]
- WO 2012028203 A [0006]
- EP 799612 A [0006]
- EP 2245128 A [0006]
- US 20140148371 A [0006]
- US 20140148372 A [0006]
- WO 2001000760 A [0006]
- WO 2003018733 A [0006]
- EP 2447349 A1 [0006]
- WO 2004013271 A1 [0006]
- US 4051058 A [0026]
- EP 2272942 A [0048]
- EP 09164872 A [0048]
- EP 2025743 A [0048]
- EP 07113156 A [0048]