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(54) HARD-SURFACE CLEANING COMPOSITIONS

REINIGUNGSMITTEL FÜR HARTE OBERFLÄCHEN

COMPOSITIONS POUR LE NETTOYAGE DE SURFACES DURES

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(56) References cited:
EP-A- 0 125 711
WO-A-94/05769
WO-A-95/14762
JP-A- 4 332 798
LU-A- 71 478
NL-A- 7 404 969
NL-A- 7 505 881

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Description

Technical Field

[0001] The present invention relates to compositions for cleaning hard-surfaces, especially in-house hard-surfaces.

Background

[0002] A variety of compositions for cleaning hard-surfaces have been disclosed in the art. Much of the focus for such compositions has been on providing outstanding cleaning on a variety of surfaces and soils. For some specialised cleaners, such as glass cleaners, much effort has additionally been devoted to the formulation of so-called "streak-free" products, i.e. products which leave no or little visible residues after use.

[0003] The object of the present invention is to formulate hard-surface cleaning compositions which clean and provide gloss to the cleaned surface. That is different from a "streak-free" composition, in that gloss additionally requires improved reflectance of light from the cleaned surface. A variety of products are commercially available for delivering gloss to surfaces, and they are disclosed for instance in US 3,960,575 and US 4,218,250. Both references recommend the use of various silicones for delivering gloss. Such compositions are not fully formulated hard-surface cleaners, so that they do not clean efficiently, and indeed the formulation of silicone in hard-surface cleaners has not shown any gloss benefits. See for instance EP 374 471 which discloses a hard-surface cleaning composition with, amongst other essentials, a silicone for improved resistance to soil redeposition.

[0004] We have now found that superior gloss on surfaces can be obtained by formulating liquid compositions according to claim 4. Indeed, it has been found that said compositions provide excellent cleaning performance on different types of stains including typical greasy stains while delivering improved gloss and less surface streaking/spotting.

[0005] An advantage of the present invention is that said compositions may be used to clean in-house hard-surfaces made of a variety of material like glazed and non-glazed ceramic tiles, vinyl, linoleum, melamine, both in diluted and neat conditions.

[0006] Another advantage of the process of cleaning hard-surfaces according to the present invention wherein the compositions herein is used in diluted form is that enhanced gloss is provided to the surfaces treated without the need of a subsequent rinsing, thereby facilitating its usage by the consumer.

[0007] US 4784 786 discloses a composition for cleaning glass which can be readily applied to and removed from a soiled glass surface to leave the surface clean and free of streaking and cloudiness. Said compositions comprise amongst other ingredients, surfactants, glycol ether, an anionic polysulfonic acid and an anhydride compound comprising an olefin-maleic anhydride copolymer. No divalent counterions are disclosed.

[0008] WO 94/26858 discloses a liquid hard-surface composition (pH 2-8) with nonionic surfactants (1-30%) and anionic polymers having an average molecular weight of less than 1 000 000. Said compositions bring a surprising initial cleaning benefit in addition to the anti-soiling benefit. Indeed, WO 94/26858 discloses that acrylic, methacrylic and maleic anhydride derivatives such as copolymers of styrene with maleic produce a streak-free finish after drying. No divalent counterions are disclosed.

[0009] EP-A-658 184 discloses liquid or gel dishwashing detergent compositions containing alkyl amphocarboxylic acid (5%-95%) and magnesium or calcium salts (0.1%-4%), said compositions having a pH in a 10% solution in water at 20°C of 7 to 10. As optional ingredients said compositions comprise co-surfactants, like nonionic surfactants (5%-95%). No carboxylate-containing polymers are disclosed. Also no hard-surfaces application is disclosed.

[0010] EP-A-162 033 discloses heavy-duty liquid detergents comprising proteolytic or amylolytic enzymes, an anionic surfactant (10%-50%), optionally other surfactants like nonionic ethoxylated surfactants (2%-25%), from 1 to 30 millimoles of calcium ions per liter of composition and detergent builders (2%-15%) like polycarboxylates including water-soluble salts of specific polymeric aliphatic polycarboxylic acids (e.g., polymers and copolymers of maleic acid). EP-A-162 033 further discloses that the level of calcium ions should be selected so that there is always some minimum level available for the enzyme, after allowing for complexation with fatty acids and the like in the composition. Sources of calcium ions are for example calcium chloride and/or calcium acetate. No hard-surface application is disclosed.

[0011] EP-A-602 179 discloses that the addition of calcium salts to compositions containing a polyhydroxy fatty acid amide, and an anionic surfactant improves the removal of greasy soils while delivering good hand mildness. Indeed, EP-A-602 179 discloses dishwashing compositions comprising an anionic surfactant (3%-95%), a polyhydroxy fatty acid amide (3%-40%) and calcium ions (0.1% to 3%). The compositions have a pH of from 5.5 to 10 in a 10% solution in water at 20°C. As optional ingredients said compositions comprise polycarboxylate polymers having a molecular weight of 750 000 to 4 000 000 (0.1%-10%). No hard-surface cleaning application is disclosed.

[0012] EP-A-670 884 discloses fully formulated liquid detergent compositions (pH 7.5-9.5) comprising a polyhydroxy fatty acid amide surfactant (5%-50%), a nonionic (5%-50%), a source of calcium (0.5%-2%) and soap. Optional ingredients are polycarboxylate builders such as copolymers of maleic anhydride with ethylene or vinyl methyl ether and

polymeric polycarboxylic dispersing agents (0.1%-7%) that can be prepared by polymerizing or copolymerizing suitable unsaturated monomers including acrylic acid, maleic acid. Acrylic/maleic-based copolymers with a molecular weight of 2 000 to 100 000 are disclosed. No hard-surface application is disclosed.

[0013] GB 1430 204 discloses compositions suitable to clean various soiled subtracts including hard-surfaces. Said compositions comprise a polymer (3%-35%) such as acrylic polymers and polycarbonates, optionally metal ions such as calcium or magnesium (0.1%-5%), and builders (0.1%-5%) such as copolymers of vinyl methyl ether and maleic anhydride, and carboxymethyl cellulose. A surfactant may be used as optional but no levels thereof are disclosed, let alone particular classes of surfactants. GB 1430 204 also discloses a process of cleaning a soiled surface, said process comprising the steps of applying to said surface said composition, allowing said composition to form a tacky film to which soils adhere, allowing said composition to dry, whereby as a result of said drying, said film fractures to form a removable residue and then removing said residue. The presence of the metal ions increases the brittleness of the film.

[0014] Actually, the benefit derivable from the use of a surfactant, a carboxylate-containing polymer and a divalent counterion in appropriate molar ratios of said polymer to said divalent counterion, in a liquid hard-surface cleaning composition, i.e. improved gloss to the surfaces treated therewith, has not been acknowledged in the prior art.

Summary of the invention

[0015] The present invention encompasses a process of cleaning hard-surfaces wherein a liquid composition having a pH of from 6 to 13 and comprising a carboxylate-containing polymer and a divalent counterion, added in the form of a non-complex salt or as one ingredient with said carboxylate-containing polymer, in a molar ratio of said polymer to said divalent counterion of from 12:1 to 1:32 and from 0.1% to 50% by weight of the total composition of a surfactant, is applied onto said surface, wherein said carboxylate-containing polymer is a cellulose derivative, a polyacrylate an acrylic/maleic-based copolymer or a mixture thereof.

[0016] The present invention also encompasses a liquid hard-surface cleaning composition having a pH of from 6 to 13 and comprising a carboxylate-containing polymer and a divalent counterion, added in the form of a non-complex salt or as one ingredient with said carboxylate-containing polymer, in a molar ratio of said polymer to said divalent counterion of from 12:1 to 1:32 and from 0.1% to 50% by weight of the total composition of a surfactant, wherein said carboxylate-containing polymer is a cellulose derivative, a polyacrylate an acrylic/maleic-based copolymer or a mixture thereof. said composition being free of a proteolytic or amylolytic enzyme and of polyhydroxy fatty acid amide.

Detailed Description of the invention

[0017] In its broadest aspect, the present invention relates to a process of cleaning hard-surfaces wherein a liquid composition comprising a carboxylate-containing polymer and a divalent counterion, added in the form of a non-complex salt or as one ingredient with said carboxylate-containing polymer, in a molar ratio of said polymer to said divalent counterion of from 12:1 to 1:32 and a surfactant, is applied onto said surfaces, wherein said carboxylate-containing polymer is a cellulose derivative, a polyacrylate, an acrylic/maleic-based copolymer or a mixture thereof.

[0018] By "hard-surfaces" it is meant herein any kind of in-house hard-surfaces with the exception of dishes and any utensiles used for the cooking and for eating/drinking. Preferred herein "hard-surfaces" has to be understood as any fixed household hard-surface including floors, walls, windows, fixtures and fittings and the like.

[0019] Said liquid composition may be applied to the surface to be cleaned in its neat form or in its diluted form.

[0020] By "diluted form" it is meant herein that said liquid composition is diluted by the user typically with water. The composition is diluted prior use to a typical dilution level of 10 to 200 times its weight of water. Usual recommended dilution level is a 1.2% dilution of the composition in water which corresponds to an active level of from 0.01% to 0.5% by weight of the resulting washing solution.

[0021] When applying said composition to the surface to be cleaned in its neat form or in a so-called concentrated form (i.e. between 10%-40% total actives), it is necessary to rinse the surface after the composition has been applied, otherwise too many visible residues are left on the surface. In this "concentrated" usage form, however, the gloss benefit provided by the compositions of the present invention is still obtained after fewer rinses than would otherwise be required when using the same composition without said surfactant or the same composition without said polymer and said divalent counterion in a molar ratio of said polymer to said divalent counterion of from 12:1 to 1:32.

[0022] In the preferred process of cleaning hard-surfaces according to the present invention where said composition is used in diluted form, there is no need to rinse the surface after application of the composition in order to obtain the gloss benefit.

[0023] In one embodiment the present invention is a liquid hard-surface cleaning composition comprising a carboxylate-containing polymer and a divalent counterion, added in the form of a non-complex salt or as one ingredient with said carboxylate-containing polymer, in molar ratio of said polymer to said divalent counterion of from 12:1 to 1:32 and from 0.1% to 50% by weight of the total composition of a surfactant, wherein said carboxylate-containing polymer is a

cellulose derivative, a polyacrylate, an acrylic maleic-based copolymer or a mixture thereof, said composition being free of a proteolytic or amylolytic enzyme and of polyhydroxy fatty acid amide.

[0024] As a first essential ingredient, the compositions according to the present invention comprise a carboxylate-containing polymer, or mixtures thereof. By "carboxylate-containing polymer" it is meant herein a polymer or copolymer comprising at least a monomeric unit which contains at least a carboxylate functionality. As carboxylate-containing polymers can be employed according to the present invention homo- or co-polymeric polyacrylates or mixtures thereof. Indeed, such carboxylate-containing polymers can be prepared by polymerizing or copolymerizing suitable unsaturated monomers, preferably in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid.

[0025] Particularly suitable polymeric polycarboxylates can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges from about 2,000 to 1,000,000, more preferably from about 10,000 to 150,000 and most preferably from about 20,000 to 100,000. Water-soluble salts of such acrylic acid polymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble polymers of this type are known materials. Use of polyacrylates of this type in detergent compositions has been disclosed, for example, in Diehl, U.S. Patent 3,308,067, issued March 7, 1967.

[0026] Acrylic/maleic-based copolymers may also be used as a preferred carboxylate-containing polymer. Such materials include the water-soluble salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form preferably ranges from about 2,000 to 100,000, more preferably from about 5,000 to 75,000, most preferably from about 7,000 to 65,000. The ratio of acrylate to maleate segments in such copolymers will generally range from about 30:1 to about 1:1, more preferably from about 10:1 to 2:1. Water-soluble salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915, published December 15, 1982. Particularly preferred is a copolymer of maleic / acrylic acid with an average molecular weight of about 70,000. Such copolymers are commercially available from BASF under the trade name SOKALAN CP5.

[0027] Other suitable carboxylate-containing polymers to be used herein include cellulose derivatives such as carboxymethylcellulose. For example carboxymethylcellulose may be used as a salt with conventional cation such as sodium, potassium, amines or substituted amines.

[0028] As a second essential ingredient, the compositions according to the present invention comprise a divalent counterion, or mixtures thereof. All divalent ions known to those skilled in the art may be used herein. Preferred divalent ions to be used herein are calcium, zinc, cadmium, nickel, copper, cobalt, zirconium, chromium and/or magnesium and more preferred are calcium, zinc and/or magnesium. Said divalent ions are added in the form of salts for example as chloride, acetate, sulphate, formate and/or nitrate. For example, calcium may be added in the form of calcium chloride, magnesium as magnesium acetate or magnesium sulphate and zinc as zinc chloride.

[0029] In one embodiment of the present invention said carboxylate-containing polymer and said divalent counterion may be added as one ingredient provided that the molar ratio of said carboxylate-containing polymer to said divalent counterion/salt is from 12:1 to 1:32.

[0030] According to the present invention, said polymer and said divalent counterion are present in the compositions for cleaning hard-surfaces herein in a molar ratio of said polymer to said divalent counterion of from 12:1 to 1:32, preferably of from 8:1 to 1:16, more preferably of from 6:1 to 1:12 and most preferably of from 4:1 to 1:6. Preferred molar ratios of said polymer to said divalent counterion are those where improved gloss is obtained in the most economic way.

[0031] By "molar ratio of said polymer to said divalent counterion" it is meant herein the number of moles of carboxylate-containing monomer to the number of moles of divalent ion. For example, in a preferred embodiment of the present invention where said carboxylate-containing polymer is an acrylic acid/maleic acid copolymer the molar ratio is stated as a range based on the theoretical molar ratio of a pure acrylic acid polymer to divalent ions and a pure maleic acid polymer to divalent ions.

[0032] Accordingly, the compositions for the cleaning of hard-surfaces according to the present invention comprise from 0.01% to 20% by weight of the total composition of said carboxylate-containing polymer, or mixtures thereof, preferably from 0.1% to 10%, more preferably from 0.1% to 5% and from 0.01 % to 4% by weight of the total composition of said divalent counterion, or mixtures thereof, preferably from 0.02% to 2%, and more preferably from 0.02% to 1%.

[0033] By "improved gloss" it is meant herein that the gloss observed, when cleaning a hard-surface according to the present invention with a composition comprising a surfactant, a carboxylate-containing polymer and a divalent counterion in a molar ratio of said polymer to said divalent counterion of from 12:1 to 1:32, is improved as compared to the gloss observed when cleaning said surface with the same composition without said surfactant, or with the same composition without said divalent counterion and said carboxylate-containing polymer in a molar ratio of said polymer to said divalent counterion of from 12:1 to 1:32. This gloss improvement is observed in both neat or diluted usage

conditions, and especially in the embodiment where the diluted usage is performed with soft water, i.e. a water with a water hardness of less than 171.5 ppm $CaCO_3$ (10 grains/gallons). This gloss benefit may be evaluated by reflectance as judged by a gloss meter and/or by a visual grading as judged by a panel of graders.

[0034] As a third essential ingredient, the compositions according to the present invention comprise a surfactant, or mixtures thereof. Said surfactant is present in the compositions according to the present invention in amounts of from 0.1% to 50% by weight of the total composition, preferably from 0.1% to 20% and more preferably of from 1% to 10%. It is said surfactant which in combination with said polymer and divalent counterion, is deposited on the surface cleaned and contributes to the gloss benefit. Surfactants to be used herein include nonionic surfactants, anionic surfactants, cationic surfactants, amphoteric surfactants, zwitterionic surfactants, and mixtures thereof.

[0035] Particularly preferred surfactants are the nonionic surfactants. Suitable nonionic surfactants for use herein include a class of compounds which may be broadly defined as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be branched or linear aliphatic (e.g. Guerbet or secondary alcohols) or alkyl aromatic in nature. The length of the hydrophilic or polyoxyalkylene radical which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements. For example, a well-known class of nonionic synthetic detergents is made available on the market under the trade name "Pluronic". These compounds are formed by condensing ethylene oxide with an hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The hydrophobic portion of the molecule which, of course, exhibits water-insolubility has a molecular weight of from about 1500 to 1800. The addition of polyoxyethylene radicals to this hydrophobic portion tends to increase the water-solubility of the molecule as a whole and the liquid character of the products is retained up to the point where polyoxyethylene content is about 50% of the total weight of the condensation product.

[0036] Other suitable nonionic synthetic detergents include :

(i) The polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to 12 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to 10 to 25 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived from polymerized propylene, diisobutylene, octane, and nonane;

(ii) Those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine products which may be varied in composition depending upon the balance between the hydrophobic and hydrophilic elements which is desired. Examples are compounds containing from about 40% to about 80% polyoxyethylene by weight and having a molecular weight of from about 5000 to about 11000 resulting from the reaction of ethylene oxide groups with a hydrophobic base constituted of the reaction product of ethylene diamine and excess propylene oxide, said base having a molecular weight of the order of 2500 to 3000;

(iii) The condensation product of aliphatic alcohols having from 8 to 18 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide, e.g., a coconut alcohol ethylene oxide condensate having from 10 to 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from 10 to 14 carbon atoms;

(iv) Trialkyl amine oxides and trialkyl phosphine oxides wherein one alkyl group ranges from 10 to 18 carbon atoms and two alkyl groups range from 1 to 3 carbon atoms; the alkyl groups can contain hydroxy substituents; specific examples are dodecyl di(2-hydroxyethyl)amine oxide and tetradecyl dimethyl phosphine oxide.

[0037] Particularly preferred surfactants include also the anionic surfactants. Suitable anionic surfactants for use herein include alkali metal (e.g., sodium or potassium) fatty acids, or soaps thereof, containing from about 8 to about 24, preferably from about 10 to about 20 carbon atoms.

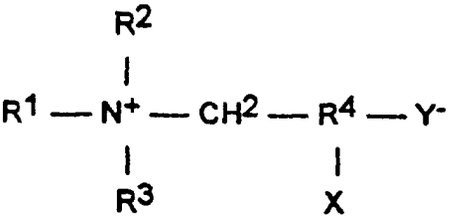
[0038] The fatty acids including those used in making the soaps can be obtained from natural sources such as, for instance, plant or animal-derived glycerides (e.g., palm oil, coconut oil, babassu oil, soybean oil, castor oil, tallow, whale oil, fish oil, tallow, grease, lard and mixtures thereof). The fatty acids can also be synthetically prepared (e.g., by oxidation of petroleum stocks or by the Fischer-Tropsch process). Alkali metal soaps can be made by direct saponification of fats and oils or by the neutralization of the free fatty acids which are prepared in a separate manufacturing process. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium and potassium tallow and coconut soaps.

[0039] The term "tallow" is used herein in connection with fatty acid mixtures which typically have an approximate carbon chain length distribution of 2.5% C14, 29% C16, 23% C18, 2% palmitoleic, 41.5% oleic and 3% linoleic (the first three fatty acids listed are saturated). Other mixtures with similar distribution, such as the fatty acids derived from

various animal tallows and lard, are also included within the term tallow. The tallow can also be hardened (i.e., hydrogenated) to convert part or all of the unsaturated fatty acid moieties to saturated fatty acid moieties. When the term "coconut" is used herein it refers to fatty acid mixtures which typically have an approximate carbon chain length distribution of about 8% C8, 7% C10, 48% C12, 17% C14, 9% C16, 2% C18, 7% oleic, and 2% linoleic (the first six fatty acids listed being saturated). Other sources having similar carbon chain length distribution such as palm kernel oil and babassu oil are included with the term coconut oil.

[0040] Other suitable anionic surfactants for use herein include water-soluble salts, particularly the alkali metal salts, of organic sulfuric reaction products having in the molecular structure an alkyl radical containing from about 8 to about 22 carbon atoms and a radical selected from the group consisting of sulfonic acid and sulfuric acid ester radicals. Important examples of these synthetic detergents are the sodium, ammonium or potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols produced by reducing the glycerides of tallow or coconut oil; sodium or potassium alkyl benzene sulfonates, in which the alkyl group contains from about 9 to about 15 carbon atoms, especially those of the types described in U.S. Pat. Nos. 2,220,099 and 2,477,383, sodium alkyl glyceryl ether sulfonates, especially those ethers of the higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfates and sulfonates; sodium or potassium salts of sulfuric acid esters of the reaction product of one mole of a higher fatty alcohol (e.g., tallow or coconut oil alcohols) and about three moles of ethylene oxide; sodium or potassium salts of alkyl phenol ethylene oxide ether sulfates with about four units of ethylene oxide per molecule and in which the alkyl radicals contain about 9 carbon atoms; the reaction product of fatty acids esterified with isothionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts of fatty acid amide of a methyl taurine in which the fatty acids, for example, are derived from coconut oil; and others known in the art, a number being specifically set forth in U.S. Pat. Nos. 2,486,921, 2,486,922 and 2,396,278.

[0041] Suitable zwitterionic detergents to be used herein comprise the betaine and betaine-like detergents wherein the molecule contains both basic and acidic groups which form an inner salt giving the molecule both cationic and anionic hydrophilic groups over a broad range of pH values. Some common examples of these detergents are described in U.S. Pat. Nos. 2,082,275, 2,702,279 and 2,255,082. Preferred zwitterionic detergent compounds have the formula



wherein R1 is an alkyl radical containing from about 8 to about 22 carbon atoms, R2 and R3 contain from 1 to 3 carbon atoms, R4 is an alkylene chain containing from 1 to about 3 carbon atoms, X is selected from the group consisting of hydrogen and a hydroxyl radical, Y is selected from the group consisting of carboxyl and sulfonyl radicals and wherein the sum of R1, R2 and R3 radicals is from 14 to 24 carbon atoms.

[0042] Amphoteric and ampholytic detergents which can be either cationic or anionic depending upon the pH of the system are represented by detergents such as dodecylbeta-alanine, N-alkyltaurines such as the one prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. Pat. No. 2,658,072, N-higher alkylaspartic acids such as those produced according to the teaching of U.S. Pat. No. 2,438,091, and the products sold under the trade name "Miranol", and described in U.S. Pat. No. 2,528,378. Additional synthetic detergents and listings of their commercial sources can be found in McCutcheon's Detergents and Emulsifiers, North American Ed. 1980.

[0043] The compositions according to the present invention are liquid hard-surface cleaning compositions. The liquid compositions of the present invention are preferably but not necessarily formulated as aqueous compositions. Aqueous compositions typically comprise from 50% to 98% by weight of the total composition of water, preferably from 60% to 95%, and more preferably from 80% to 95%.

[0044] The compositions according to the present invention have a pH of from 6 to 13, preferably of from 6.5 to 12, and more preferably of from 7 to 11. The pH of the compositions herein can be adjusted by any of the means well-known to the man skilled in the art such as addition of NaOH, KOH, K2CO3, Na2CO3 and the like.

[0045] The compositions herein can further comprise a variety of optional ingredients. Suitable optional ingredients for use herein include builders, chelants, solvents, buffers, bactericides, hydrotropes, colorants, stabilizers and/or perfumes.

[0046] Suitable perfumes to be used herein include materials which provide an olfactory aesthetic benefit and/or

cover any "chemical" odor that the product may have. The main function of a small fraction of the highly volatile, low boiling (having low boiling points), perfume components in these perfumes is to improve the fragrance odor of the product itself, rather than impacting on the subsequent odor of the surface being cleaned. However, some of the less volatile, high boiling perfume ingredients provide a fresh and clean impression to the surfaces, and it is desirable that these ingredients be deposited and present on the dry surface. Perfume ingredients can be readily solubilized in the compositions, for instance by the nonionic detergent surfactants.The perfume ingredients and compositions suitable to be used herein are the conventional ones known in the art. Selection of any perfume component, or amount of perfume, is based solely on aesthetic considerations.

[0047] Suitable perfume compounds and compositions can be found in the art including U.S. Pat. Nos. : 4,145,184, Brain and Cummins, issued March 20, 1979; 4,209,417, Whyte, issued June 24, 1980; 4,515,705, Moeddel, issued May 7, 1985; and 4,152,272, Young, issued May 1, 1979. In general, the degree of substantivity of a perfume is roughly proportional to the percentages of substantive perfume material used. Relatively substantive perfumes contain at least 1%, preferably at least 10%, substantive perfume materials.Substantive perfume materials are those odorous compounds that deposit on surfaces via the cleaning process and are detectable by people with normal olfactory acuity. Such materials typically have vapor pressures lower than that of the average perfume material. Also, they typically have molecular weights of about 200 and above, and are detectable at levels below those of the average perfume material.Perfume ingredients useful herein, along with their odor character, and their physical and chemical properties, such as boiling point and molecular weight, are given in "Perfume and Flavor Chemicals (Aroma Chemicals)," Steffen Arctander, published by the author, 1969.

[0048] Examples of the highly volatile, low boiling, perfume ingredients are : anethole, benzaldehyde, benzyl acetate, benzyl alcohol, benzyl formate, isobornyl acetate, camphene, ciscitral (neral), citronellal, citronellol, citronellyl acetate, para-cymene, decanal, dihydrolinalool, dihydromyrcenol, dimethyl phenyl carbinol, eucaliptol, geranial, geraniol, geranyl acetate, geranyl nitrile, cis-3-hexenyl acetate, hydroxycitronellal, d-limonene, linalool, linalool oxide, linalyl acetate, linalyl propionate, methyl anthranilate, alpha-methyl ionone, methyl nonyl acetaldehyde, methyl phenyl carbinyl acetate, laevo-menthyl acetate, menthone, iso-menthone, mycrene, myrcenyl acetate, myrcenol, nerol, neryl acetate, nonyl acetate, phenyl ethyl alcohol, alpha-pinene, beta-pinene, gamma-terpinene, alpha-terpineol, beta-terpineol, terpinyl acetate, and vertenex (para-tertiary-butYl cyclohexyl acetate). Some natural oils also contain large percentages of highly volatile perfume ingredients. For example, lavandin contains as major components : linalool; linalyl acetate; geraniol; and citronellol. Lemon oil and orange terpenes both contain about 95% of d-limonene.

[0049] Examples of moderately volatile perfume ingredients are : amyl cinnamic aldehyde, iso-amyl salicylate, beta-acaryophyllene, cedrene, cinnamic alcohol, coumarin, dimethyl benzyl carbinyl acetate, ethyl vanillin, eugenol, isoeug-enol, flor acetate, heliotropine, 3-cis-hexenyl salicylate, hexyl salicylate, lilial (para-tertiarybutyl-alpha-methyl hydrocinnamic aldehyde), gamma-methyl ionone, nerolidol, patchouli alcohol, phenyl hexanol, beta-selinene, trichloromethyl phenyl carbinyl acetate, triethyl citrate, vanillin, and veratraldehyde. Cedarwood terpenes are composed mainly of alpha-cedrene, beta-cedrene, and other C15H24 sesquiterpenes.

[0050] Examples of the less volatile, high boiling, perfume ingredients are : benzophenone, benzyl salicylate, ethylene brassylate, galaxolide (1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-cyclopenta-gama-2-benzopyran), hexyl cinnamic aldehyde, lyral (4-(4-hydroxy-4-methyl pentyl)-3-cyclohexene-10-carboxaldehyde), methyl cedrylone, methyl dihydro jasmonate, methyl-beta-naphthyl ketone, musk indanone, musk ketone, musk tibetene, and phenylethyl phenyl acetate.

[0051] Selection of any particular perfume ingredient is primarily dictated by aesthetic considerations.

[0052] The compositions herein may comprise a perfume ingredient, or mixtures thereof, in amounts up to 5.0% by weight of the total composition, preferably in amounts of 0.1 % to 1.5%.

[0053] Another class of optional compounds are chelating agents such as those selected from the group of aminophosphonates. Suitable amino phosphonate compounds for use herein include amino alkylene poly (alkylene phosphonate), alkali metal ethane 1-hydroxy diphosphonates, nitrilo trimethylene phosphonates, ethylene diamine tetra methylene phosphonates, and diethylene triamine penta methylene phosphonates. The phosphonate compounds may be present either in their acid form or as salts of different cations on some or all of their acid functionalities. Preferred amino phosphonate chelant to be used herein is diethylene triamine penta methylene phosphonate. Such phosphonate chelant is commercially available from Monsanto under the trade name DEQUEST®.

[0054] Chelants can be incorporated in the compositions herein in amounts ranging from 0.0% to 10.0% by weight of the total composition, preferably 0.1 % to 5.0%.

[0055] The present invention will be further illustrated by the following examples.

Examples

[0056] The following compositions were made by mixing the listed ingredients in the listed proportions. All proportions are % by weight of the total composition. These compositions were used neat and diluted to clean hard-surfaces like

floors. Excellent cleaning performance and excellent gloss were delivered to the surfaces cleaned.

Compositions (weight%)	1	2	3
C7/C9/C11 EO6.5	3.0	3.0	3.0
C12/C13 EO3	1.0	1.0	1.0
C13/C15 EO3O	2.0	2.0	2.0
Palm Kernal Fatty Acid	0.4	0.4	0.4
Perfume	0.45	0.45	0.45
Sokolan® CP5*	1.0	0	0
Carboxymethyl cellulose	0	1.0	0
Primal® B 924***	0	0	1.0
CaCl2.2H2O	1.0	1.0	1.0
Water and minors	--------up to 100%--------		
pH	10.5	10.5	10.5

* Maleic acid-acrylic acid copolymer (MW = 70 000)

** Polycarboxylate copolymer (MW = 50 000)

[0057] The molar ratio of said carboxylate-containing polymer to calcium ions in examples 1 to 3 is from 2.1:1 to 1.2:1.

Compositions (weight%)	4	5	6	7	8	9	10
C7/C9/C11 EO6.5	3.0	3.0	3.0	3.0	3.0	0.0	0.0
C12/C13 EO3	1.0	1.0	1.0	1.0	1.0	1.0	1.0
C13/C15 EO3O	2.0	2.0	2.0	2.0	2.0	4.0	4.0
Palm Kernal Fatty Acid	0.4	0.4	0.4	0.4	0.4	0.4	0.0
Perfume	0.45	0.45	0.45	0.45	0.45	0.3	0.3
Sokolan CP5*	1.0	1.0	1.0	1.0	3.0	0.5	0.5
CaCl2.2H2O	0.5	0	0	0.5	1.0	1.0	0.0
MgSO4.7H2O	0	1.68	0	0	0	0	0.5
ZnCl2	0	0	0.93	0	0	0	0
Water and minors	----------up to 100%----------						
pH	10.5	10.5	10.5	10.5	10.5	10.5	10.5

* Maleic acid-acrylic acid copolymer (MW = 70 000)

[0058] The molar ratio of said carboxylate-containing polymer to said divalent ions in examples 5 and 8 is from 4.2:1 to 2.4:1, in examples 6 and 7 is from 2.1:1 to 1.2:1, in example 9 is from 6.3:1 to 3.6:1, in example 10 is from 1.1:1 to 1:1.7, and from 3.5:1 to 2.1:1 in example 11.

Claims

1. A process of cleaning a hard-surface wherein a liquid composition having a pH of from 6 to 13 and comprising a carboxylate-containing polymer and a divalent counterion, added in the form of a non-complex salt or as one ingredient with said carboxylate-containing polymer, in a molar ratio of said polymer to said divalent counterion of from 12:1 to 1:32 and from 0.1 % to 50% by weight of the total composition of a surfactant, is applied onto said surface, wherein said carboxylate-containing polymer is a cellulose derivative, a polyacrylate, an acrylic/maleic-based copolymer, or a mixture thereof.

2. A process of cleaning a hard-surface according to claim 1 wherein said composition is applied onto said surface after having been diluted with water.

3. A process according to claim 2 wherein said surface is not rinsed after said composition has been applied.

4. A liquid hard-surface cleaning composition having a pH of from 6 to 13 and comprising a carboxylate-containing

polymer and a divalent counterion, added in the form of a non-complex salt or as one ingredient with said carboxylate-containing polymer, in a molar ratio of said polymer to said divalent counterion of from 12:1 to 1:32, and from 0.1% to 50% by weight of the total composition of a surfactant, wherein said carboxylate-containing polymer is a cellulose derivative, a polyacrylates, an acrylic/maleic-based copolymer, or a mixture thereof, said composition being free of a proteolytic or amylolytic enzyme and of polyhydroxy fatty acid amide.

5. A composition or process according to any of the preceding claims wherein said composition is an aqueous liquid composition having a pH of from 6.5 to 12 and preferably of from 7 to 11.

6. A composition or process according to any of the preceding claims wherein said carboxylate-containing polymer is carboxymethylcellulose, or an acrylic acid-based polymer with an average molecular weight in its acidic form preferably of from 2 000 to 1 000 000, or an acrylic/maleic based copolymer wherein the ratio of acrylate to maleate monomers ranges from 30:1 to 1:1 with an average molecular weight preferably of from 2000 to 100 000, or mixtures thereof.

7. A composition or process according to any of the preceding claims wherein said divalent counterion is a salt of calcium, zinc, cadmium, nickel, copper, cobalt, zirconium, chromium, magnesium, or-mixtures thereof, and preferably is calcium chloride and/or magnesium sulphate and/or zinc chloride.

8. A composition or process according to any of the preceding claims wherein said polymer and said divalent counterion are present in a molar ratio of said polymer to said divalent counterion of from 8:1 to 1:16, preferably of from 6:1 to 1:12 and more preferably 4:1 to 1:6.

9. A composition or process according to any of the preceding claims wherein said composition further comprises an optional ingredient selected from the group of perfumes, chelating agents, builders, solvents, buffers, bactericides, hydrotropes, colorants, or mixtures thereof.

10. A composition or process according to any of the preceding claims wherein said surfactant is selected from the group of nonionic surfactants, anionic surfactants, zwitterionic surfactants, amphoteric surfactants, cationic surfactants and mixtures thereof, and preferably is a nonionic surfactant or mixtures thereof.

11. A composition or process according to any of the preceding claims wherein said composition comprises from 0.1% to 20% of the total composition of said surfactant or mixtures thereof, and preferably from 1% to 10%.

Patentansprüche

1. Verfahren zum Reinigen einer harten Oberfläche, bei dem eine flüssige Zusammensetzung mit einem pH von 6 bis 13 umfassend ein carboxylathaltiges Polymer und ein zweiwertiges Gegenion, welches in Form eines Nichtkomplex-Salzes oder als ein Bestandteil mit dem carboxylathaltigen Polymer zugesetzt ist, in einem Molverhältnis von Polymer zu zweiwertigem Gegenion von 12 : 1 bis 1 : 32, und 0,1 bis 50 Gew.-% der gesamten Zusammensetzung eines Tensids, auf die Oberfläche aufgebracht wird. wobei das carboxylathaltige Polymer ein Cellulosederivat, ein Polyacrylat, ein Acrylsäure-/Maleinsäure-basiertes Copolymer oder eine Mischung hiervon ist.

2. Verfahren zum Reinigen einer harten Oberfläche nach Anspruch 1, wobei die Zusammensetzung auf die Oberfläche aufgebracht wird, nachdem sie mit Wasser verdünnt worden ist.

3. Verfahren nach Anspruch 2, wobei die Oberfläche nicht gespült wird, nachdem die Zusammensetzung aufgebracht worden ist.

4. Flüssige Reinigungsmittelzusammensetzung für harte Oberflächen mit einem pH von 6 bis 13 umfassend ein carboxylathaltiges Polymer und ein zweiwertiges Gegenion, das in Form eines Nichtkomplex-Salzes oder als ein Bestandteil mit dem carboxylathaltigen Polymer zugesetzt ist, in einem Molverhältnis von Polymer zu zweiwertigem Gegenion von 12 : 1 bis 1 : 32. und 0.1 bis 50 Gew.-% der gesamten Zusammensetzung eines Tensids, wobei das carboxylathaltige Polymer ein Cellulosederivat, ein Polyacrylat, ein Acrylsäure-/Maleinsäure-basiertes Copolymer oder eine Mischung hiervon ist, wobei die Zusammensetzung frei ist an einem proteolytischen oder amylolytischen Enzym und an Polyhydroxyfettsäureamid.

5. Zusammensetzung oder Verfahren nach mindestens einem der vorangehenden Ansprüche, wobei die Zusammensetzung eine wäßrige flüssige Zusammensetzung mit einem pH von 6,5 bis 12, und vorzugsweise 7 bis 11, ist.

6. Zusammensetzung oder Verfahren nach mindestens einem der vorangehenden Ansprüche, wobei das carboxylathaltige Polymer Carboxymethylcellulose oder ein Polymer auf Acrylsäurebasis mit einem Durchschnittsmolekulargewicht in seiner Säureform von vorzugsweise 2000 bis 1000000. oder ein Copolymer auf Acryl-/Maleinsäurebasis. worin das Verhältnis von Acrylat- zu Maleat-Monomeren im Bereich von 30 : 1 bis 1 : 1 liegt, mit einem Durchschnittsmolekulargewicht von vorzugsweise 2000 bis 100000, oder Mischungen hiervon sind.

7. Zusammensetzung oder Verfahren nach mindestens einem der vorangehenden Ansprüche, wobei das zweiwertige Gegenion ein Salz von Calcium, Zink, Cadmium, Nickel, Kupfer, Cobalt, Zirkon, Chrom, Magnesium oder Mischungen hiervon, und vorzugsweise Calciumchlorid und/oder Magnesiumsulfat und/oder Zinkchlorid ist.

8. Zusammensetzung oder Verfahren nach mindestens einem der vorangehenden Ansprüche, wobei das Polymer und das zweiwertige Gegenion in einem Molverhältnis von Polymer zu zweiwertigem Gegenion von 8 : 1 bis 1 : 16, vorzugsweise 6 : 1 bis 1 : 12 und weiter vorzugsweise 4 : 1 bis 1 : 6, vorliegen.

9. Zusammensetzung oder Verfahren nach mindestens einem der vorangehenden Ansprüche. wobei die Zusammensetzung weiterhin einen wahlweisen Bestandteil umfaßt, gewählt aus der Gruppe der Parfüme, Komplexbildner. Bullder, Lösungsmittel, Puffer, Bakterizide, Hydrotrope, Färbemittel oder Mischungen hiervon.

10. Zusammensetzung oder Verfahren nach mindestens einem der vorangehenden Ansprüche, wobei das Tensid gewählt ist aus der Gruppe der nichtionischen Tenside, anionischen Tenside, zwitterionischen Tenside, amphoteren Tenside, kationischen Tenside und Mischungen hiervon, und vorzugsweise ein nichtionisches Tensid oder Mischungen hiervon sind.

11. Zusammensetzung oder Verfahren nach mindestens einem der vorangehenden Ansprüche, wobei die Zusammensetzung 0.1% bis 20% der gesamten Zusammensetzung des Tensids oder Mischungen hiervon, und vorzugsweise 1% bis 10%, umfaßt.

Revendications

1. Procédé de nettoyage d'une surface dure, dans lequel une composition liquide ayant un pH de 6 à 13 et comprenant un polymère contenant un carboxylate et un contre-ion divalent, ajouté sous la forme d'un sel non-complexe ou sous forme d'un seul ingrédient avec ledit polymère contenant un carboxylate, dans un rapport molaire dudit polymère audit contre-ion divalent de 12:1 à 1:32, et 0,1% à 50% en poids de la composition totale d'un tensioactif, est appliquée sur ladite surface, où ledit polymère contenant un carboxylate est un dérivé de cellulose, un polyacrylate, un copolymère à base d'acrylique/maléique ou un mélange de ceux-ci.

2. Procédé de nettoyage d'une surface dure selon la revendication 1, dans lequel ladite composition est appliquée sur ladite surface après avoir été diluée avec de l'eau.

3. Procédé selon la revendication 2, dans lequel ladite surface n'est pas rincée après que ladite composition a été appliquée.

4. Composition liquide de nettoyage de surfaces dures ayant un pH de 6 à 13 et comprenant un polymère contenant un carboxylate et un contre-ion divalent, ajouté sous la forme d'un sel non-complexe ou sous forme d'un seul ingrédient avec ledit polymère contenant un carboxylate, dans un rapport molaire dudit polymère audit contre-ion divalent de 12:1 à 1:32, et 0,1% à 50%, en poids de la composition totale, d'un tensioactif, où ledit polymère contenant un carboxylate est un dérivé de cellulose, un polyacrylate, un copolymère à base d'acrylique/maléique ou un mélange de ceux-ci, ladite composition étant dépourvue d'enzyme protéolytique ou amylolytique et d'amide d'acide gras polyhydroxylé.

5. Composition ou procédé selon l'une quelconque des revendications précédentes, où ladite composition est une composition liquide aqueuse ayant un pH de 6,5 à 12 et préférentiellement de 7 à 11.

6. Composition ou procédé selon l'une quelconque des revendications précédentes, où ledit polymère contenant un

carboxylate est la carboxyméthylcellulose, ou un polymère à base d'acide acrylique ayant un poids moléculaire moyen sous sa forme acide compris de préférence entre 2000 et 1 000 000, ou un copolymère à base d'acrylique/maléique dans lequel le rapport des monomères acrylate à maléate est compris entre 30:1 et 1:1 avec un poids moléculaire moyen compris de préférence entre 2000 et 100 000, ou des mélanges de ceux-ci.

7. Composition ou procédé selon l'une quelconque des revendications précédentes, où ledit contre-ion divalent est un sel de calcium, de zinc, de cadmium, de nickel, de cuivre, de cobalt, de zirconium, de chrome, de magnésium, ou des mélanges de ceux-ci, et est de préférence le chlorure de calcium et/ou le sulfate de magnésium et/ou le chlorure de zinc.

8. Composition ou procédé selon l'une quelconque des revendications précédentes, où ledit polymère et ledit contre-ion divalent sont présents dans un rapport molaire dudit polymère audit contre-ion divalent de 8:1 à 1:16, de préférence de 6:1 à 1:12 et plus préférentiellement de 4:1 à 1:6.

9. Composition ou procédé selon l'une quelconque des revendications précédentes, où ladite composition contient en outre un ingrédient optionnel choisi dans le groupe des parfums, des agents chélatants, des adjuvants, des solvants, des tampons, des bactéricides, des hydrotropes, des colorants, ou des mélanges de ceux-ci.

10. Composition ou procédé selon l'une quelconque des revendications précédentes, où ledit tensioactif est choisi dans le groupe des tensioactifs non ioniques, des tensioactifs anioniques, des tensioactifs zwittérioniques, des tensioactifs amphotères, des tensioactifs cationiques, et leurs mélanges, et de préférence est un tensioactif non ionique ou un mélange de tensioactifs non ioniques.

11. Composition ou procédé selon l'une quelconque des revendications précédentes, où ladite composition contient 0,1% à 20%, rapporté à la composition totale, dudit tensioactif ou mélange desdits tensioactifs, et de préférence 1% à 10%.